THE ART AND PRINCIPLES OF CHEMISTRY

BY THE SAME AUTHOR

THE TEACHING OF SCIENTIFIC METHOD.
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ESSAYS ON THE
ART AND PRINCIPLES OF CHEMISTRY

including the

FIRST MESSEL MEMORIAL LECTURE

by

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SEMPER ALIQUID CERTI
PROPONENDUM EST

1927

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YE *are all the children of light and the children of the day. Therefore let us not sleep as do others but let us watch and be sober. Quench not the spirit. Despise not prophesyings. Prove all things ; hold fast that which is good.*

PAUL TO THE THESSALONIANS

TO

MY SEVEN GRANDSONS AND MY SEVEN GRANDDAUGHTERS,
HOPING THAT ONE OR MORE MAY DEVELOP THE
INDIVIDUALITY TO THINK FOR HIM OR HERSELF
AND NOT BOW THE KNEE TO
AUTHORITY

PREFATORY NOTE

My desire in publishing these essays is to emphasise the need to make our practice in chemistry scientific and that we be ever mindful of the caution conveyed in Bacon's words (*Novum Organum*, XLVI, XLVII):

"The human understanding when it has once adopted an opinion (either as being the received opinion or as being agreeable to itself) draws all things else to support and agree with it. And though there be a greater number and weight of instances to be found on the other side, yet these it either neglects and despises or else by some distinction sets aside and rejects: in order that by this great and pernicious pre-determination the authority of its former conclusions may remain inviolate."

"The human understanding is moved by those things most which strike and enter the mind simultaneously and suddenly and so fill the imagination and then it feigns and supposes all other things to be somehow, though it cannot see how, similar to those few things by which it is surrounded. But for that going to and fro to remote and heterogeneous instances, by which axioms are tried as in the fire, the intellect is altogether slow and unfit, unless it be forced thereto by severe laws and overruling authority."

H. E. A.

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I *and all around me are fearfully and wonderfully made; marvellous are Thy works and that my soul knoweth right well.*

PSALM CXXXIX (Improved by Ruskin).

O Hamlet, speak no more:
Thou turn'st mine eyes into my very soul
And there I see such black and grained spots
As will not leave their tinct.

INTRODUCTION

Mr. Aldous Huxley, grandson of the great Huxley, who was distinguished not only in science but as a concise writer of forceful English, told us some time ago that he never moved without a plentiful supply of optical glass and that he always carried with him, on his travels, a volume of the twelfth half-size edition of the *Encyclopædia Britannica.* I am reminded how, in my early days, a noted chemical expert, a popular water analyst, Dr. Meymot Tidy, advised all to carry, as constant travelling companion, a two-foot tube, into which water could be filled and looked through, to judge of its colour and hence its potability. Those were times, nearly sixty years ago, when people in England, having lost their affection for beer at breakfast, were beginning to be particular about water and were soon to lead others, even the Americans, to consider its quality. The use to which Mr. Huxley puts the *Encyclopædia* seems to be less beneficent than that to which lovers of wholesome water were counselled to put the two-foot tube, as he remarks—"that one does not oneself go mad or become so in the process of reading the *Encyclopædia*, a mine of useless and unrelated knowledge, is due to the fact that one forgets." The "optical glass" he carried with him, also, it seems, was put to little more than introspective use. Recently, in discoursing of his travels, he has told us much of himself but little of what he saw: seeing, like reading, is forgetting, it appears. This is a habit of writers of which the *Encyclopædia* should cure them—if they could read it with understanding. Herein

lies the crux, perhaps. Without going mad in reading it, I have more nearly approached that state in writing for it—particularly in the effort to be clear and concise, a state unknown to the modern essayist and professional man of words which, therefore, perhaps may incite him to dementia. Having contributed articles on Chemistry to four of five successive editions, I can speak with some experience and myself incline to the view that articles in it are often little short of maddening, because of their ultra-professional, technical character. If what we are pleased to call science ever become a public possession, it will only be when writers advisedly seek to make themselves interesting and understood by the general reading public. Unfortunately, the art of writing seems to be the art of saying much about little or nothing: when there is something to be said, it becomes difficult. In our camp of science, there is no discipline of rhetoric. Our schools make no attempt to give training in the proper use of our language. Instead of requiring boys to describe what they see, they ask them to write essays upon nothing in particular. Teachers of science, more especially, pay no regard to the art of clear and concise expression. Workers in science are more often than not selfishly and thoughtlessly unmindful of their duty to make themselves understood. No literary standard prevails among us. We have not merely to mend but must end this our condition of incompetence. The States of Europe are sufficiently kept apart by a variety of languages. The States of Science, which are still more numerous and unrelated, are not only disconnected but unsympathetic, because each uses its special jargon without thought of its neighbour. We need to know and use the vulgar tongue.

My first article in the *Encyclopædia*, published in

1876, in the ninth edition, covering pages 467 to 544 in Volume V, was a comprehensive, curt conspectus of the elements, arranged in groups, following Mendeléeff's great generalisation, establishing a periodic relationship between them, which some of us who were in sympathy with the organic side already regarded as proof incontrovertible, that, though they were called elements, in reality they were compounds—a conclusion fully justified in recent times: owing to Moseley's inspired use of X-rays in fixing their serial position, by the supreme courage and genius displayed by Rutherford in interpreting Radioactivity, by J. J. Thomson's masterly pioneer electro-ballistic studies, followed by Aston's great confirmatory experimental development of Thomson's method, last but not least by J. J. Thomson's revelation of the significance of Crookes' observations and the consequent birth of the electron.

Following the lead given by Josiah Cooke (1872) in his *New Chemistry*, Avogadro's Theorem was set out in my article as the generalisation underlying the determination of all molecular and atomic weights and, therefore, as being at the root of the entire symbolic system of formulæ used by chemists in representing molecular composition and molecular interactions. Attention was specially directed to thermo-chemical relationships.

The only element I did not consider was Carbon, as Organic Chemistry was dealt with by another pen.

I had previously written a primer of Organic Chemistry, which was published in 1874. As I had also begun work upon a new edition of *Miller's Organic Chemistry* (published in 1880), my attention was closely directed to my subject at that time. The account I gave of the condition of chemistry in the *Encyclopædia* may be

taken as a fair expression of the opinions which then prevailed. We were then several years short of the dawn of the period when Physical Chemistry unfortunately began to be written up as a separate subject. Ostwald's *Zeitschrift für Physikalische Chemie* first appeared in 1884. Chemistry was still a laboratory subject—students were trained to use their hands and to be exact workers. Chemists were few and they were mostly individualists and inclined to be critical and even faithless—in the early 'seventies we were even not all convinced that there were atoms.

Perhaps unfortunately, in the interval, chemistry is become a popular and a paying subject—far too many have wandered into its ranks—too many, because the proper temperament has been lacking; as a consequence the methods of treatment adopted have too often been unpractical. The real chemical work has been mostly done in the factory-laboratory, where inexact and incomplete work cannot be tolerated—as things have to be made economically and of sufficiently good quality to be saleable.

Chemistry is a branch of Natural History, better said of Natural Knowledge or *Naturkunde*—to use the beautiful German word. It is the study of the materials of which our earth is made; it is the study of ourselves, as well as of all living things—the study of life. Surely, it is for every one to make some attempt to grasp its methods, to ponder its results, to appreciate its multitudinous messages.

No mere formal study will suffice. In one of his essays, in which he considers Wordsworth's *Prelude*, Earl Grey of Falloden draws attention to the firm conviction the poet had, that it is not through knowledge that we grow—unless that knowledge be accompanied by freedom; that great, pure, exalted thoughts are due

not to knowledge but to right or elevated feeling. Quoting the lines:

> One impulse from a vernal wood
>   May teach you more of man,
> Of moral evil and of good,
>   Than all the sages can.

he remarks that this does not mean that "the vernal wood" consciously taught him: it means that, looking on the vernal wood, he was raised to heights of sensitive feeling without which he would not have had the great thoughts that inspired his poetry.

So it is in chemistry—feeling must go with fact. The would-be chemist can only learn to be a chemist by handling materials and lovingly studying their characters —each in turn must be the "vernal wood" for which he gains "sensitive feeling"—a full understanding of its psychology: each different molecule has a psyche of its own. Chemistry is not the dull set of mere facts and formulae ill set out in the text-books—which with few exceptions are soulless: it is a living subject.

My second article, in the tenth (supplementary) edition of the *Encyclopædia*, published in 1902, was a closely written survey of the great progress made in the interval 1875 to 1900, covering pages 708 to 746. Attention was drawn to the importance of the discovery of new elements, especially of Helium and its allies and of Radium. The classification of the elements was rather fully discussed and I had the temerity to give a "visionary" table in which these were not only grouped periodically but, for the first time, in rather a special manner, foreshadowing the possible passage from one to another by an increment of a single unit of mass, which was subsequently to be justified by Aston's

discovery and apparently also by Rutherford's cruel treatment of nitrogen: he is supposed to have knocked a spot of hydrogen off the atom. The idea in my mind, at that time, was that this "unit difference" was the equivalent of the difference $CH_2 = 14$ between homologous carbon compounds. This is clearly the physicist's conception to-day but the iron of chemistry is not yet sufficiently entered into his soul for him to realise that, in what he has been pleased to call isotopes, he is dealing with a series of intimately related homologues, not with one element, just as the motorist uses not one hydrocarbon—petrol—but a mixture of closely related hydrocarbons—hexane C_6H_{14}, Heptane C_7H_{16}, etc. To assert that the isotopes are identical in properties is absurd: they differ in mass and, therefore, must differ in other respects—but the difference in mass being small, other properties will also not vary to any marked extent. Chemically speaking, the strictly homologous terms of the C_nH_{2n+2} series are alike: the differences are practically those of mass.

The structure assigned to "elementary matter" by physicists is also not in full harmony with our chemical outlook. They are thought of as made up of protons and electrons—the protons as lumped together in a nucleus, in numbers corresponding with the serial number, with light-heeled electrons moving around them in orbits, in numbers varying from 1 to 8 or maybe 32 in each orbit. The concept seems too "simple" to satisfy the facts—it is too obviously derived from living in a cubicle and an adaptation of planetary theory.

This criticism, at least, is permissible, without going so far as to say, with Mr. Bertrand Russell, that electrons and protons, like the soul, are logical fictions. We have far too little knowledge of the electron and its attach-

ments; the "free use" now made of the concept has yet to be justified experimentally. The extrusion of Helium, time after time, from radioactive materials, seems to be an indication of more specific structure, even of the presence of definite groups or "radicles" within the "elementary" system. Such materials are clearly helides: the helium in them is at least a bivalent radicle. The chemist is insensibly reminded, by such behaviour, of the polybenzenoid hydrocarbons. Being innocent of chemistry—physicists are simple-minded folk and will jump at any suggestion issued with authority—mathematicians, we know, will make a show with any speculation.

A topic of importance discussed in 1902 was that of Molecular Weight—again a clear concept not yet fully grasped by the physicist, who makes no proper distinction between the molecule (the acting dynamic unit) and the atom (the elementary unit). The new methods then coming into use in determining molecular weight in the liquid state were specially considered.

Valency and residual affinity were rather fully discussed and the difficulty was emphasised of explaining this latter property, particularly the insufficiency of the explanation the Helmholtz atomic charge affords. The present-day electronic hypothesis of valency is at most a materialisation of this and carries us no further. I formed the view in 1902, that the difference between the two forms of affinity, although a very real one, was one of order—one of quality rather than quantity. Perhaps this is going too far. Maybe, residual affinity is an electro-magnetic effect rather than directly electronic, if affinity be electronic in its origin. A chemist has little right to speculate on such matters but electronic speculation leaves us so cold thereon that we

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cannot but proclaim our wants, in the hope that, some day perhaps, physicists will grow to understand us a little and come to our rescue. The feeble attempts to solve the puzzle coming from our side are scarcely to be taken seriously—we have as yet *no* feeling for such matters. The chemists who are dabbling in electrons are obviously far from equipped with the necessary chemical feeling, let alone the mathematical. We need to gain far deeper inspiration within our own vernal woods before attempting to ascend into mountains held by another race, probably losing ourselves in quagmires on the way.

In any case, schoolboys should be kept away from the maze of electronics. To-day, they are siffling electrons, whilst knowing nothing of oxygen; the ancient universities of Oxford and Cambridge, which should have some sense of proportion, are encouraging the vicious practice by questions set in the scholarship examinations.

Isomerism was another topic that I considered rather fully, particularly with relation to the Le Bel-van't Hoff geometrical hypothesis put forward in 1874, applying it especially to the sugars. I summarised the marvellous work of Emil Fischer, as showing the progress made in determining the intimate molecular structure of a group of no less than sixteen isomerides—the greatest feat of exact imagination, fully controlled by laboratory study, on record. In this section, the phenomena of metamerism (inaptly labelled tautomerism by many) or reversible isomeric change were specially considered. Then the various hydrocarbon series were discussed, including the polymethylenes, a group then coming into prominence as a subject of study.

Chemical Change was considered at length. This

involved both a statement of my own views set forth in 1885 and subsequent years and also a discussion of the sufficiency of the ionic dissociation hypothesis, of which I have always been a consistent opponent, holding it to be both absurd and unjustified. Still, though now discredited, it has held the field these forty years past and the books are filled with it: not a few of the teachers in responsible positions, having never followed melancholy Jacques into the vernal woods of our science but merely coquetted with arithmetical Audreys on their fringe, simply cannot read any other language; they can only speak in terms of the ionic tongue and make the hydrogen ion the object of their slavish worship.

Unfortunately, in studying chemistry, through some streak of original sin in my composition, I have developed into one of those noxious people who not only dare to have opinions of their own but even to express them. This is the sin unforgivable. Chemists are human beings and, like other people, desire to live a quiet life—their chemistry is usually a mere shift of diaphanous material thinner than any *crêpe de Chine*. To be asked to think about what they are doing is boring—it isn't done in polite circles. Let somebody do the thinking for them; they will be happy to accept the lead that is given, without making any fuss. As in politics, the leader is an accident. Talking usually does the trick. About forty years ago a talkative Professor of Chemistry, who not only talked but also wrote and wrote well, discovered himself in Ostwald. He talked people into believing first in Arrhenius and then in van't Hoff, two impulsive young people, inexperienced as chemists, who had the genius to start thinking for themselves, though on rather loose premises. Ostwald made himself their henchman and trumpeter. He wrote books

about them and started a journal to carry on the cult? He then founded not a mere Mustard Club but an Ionic Suicide Club—a molecular Ku-Klux-Klan. To-day, he would have found his level more remuneratively as an advertising agent: in making people buy goods that are not good for them.

The function of the text-book writer should be other than that of the advertising agent. He is not a mere salesman's advocate but rather an appraisor of values. It is not his office to advertise X-street alone as the one to shop in: no, whilst pointing out as fully as maybe the advantages it offers, also to make clear its limitations and the facilities afforded elsewhere of making this or that purchase, perhaps, even with greater advantage.

Whatever the subject, the student asks for a Bible—so soon as he has one in his hands and has superficially mastered its gospel he believes in it. Faith is an affectation that is built into the very marrow of our bones. It is usually unhinged only by some special, more or less severe personal experience—rarely if ever by argument. Most people to understand a subject at all must directly deal in it. Some elderly people like myself, brought up on the wholesome tradition of Hell Fire, can remember how difficult it was to shake off the idea of his Satanic Majesty's constant attendance at one's elbow. Arrhenic ions have been so infused into the blood of our youth that they are part of their very being.

To-day confusion is worse confounded, owing to the fact that physicists have thoughtlessly and most wickedly stolen the term *ion* from us and use it in a special way of their own. To them the ion is definitely the free, electrically charged, moving particle—a simple ballistic unit, though some go so far as to picture its existence in solids, like salt.

Faraday, in 1834, defined the term in the following words:

"Finally, I require a term to express those bodies which can pass to the *electrodes* or, as they are usually called, the poles. Substances are frequently spoken of as being *electro-negative* or *electro-positive*, according as they go under the supposed influence of a direct attraction to the positive or negative pole. But these terms are much too significant for the use to which I should have put them; for though the meanings are perhaps right, they are only hypothetical and may be wrong; and then, through a very imperceptible but still very dangerous because continual influence, they do great injury to science by contracting and limiting the habitual views of those engaged in pursuing it. I propose to distinguish such bodies by calling those *anions* which go the *anode* of the decomposing body and those passing to the *cathode cations*; and when I have occasion to speak of these together, I shall call them *ions*. Thus the chloride of lead is an *electrolyte* and when *electrolysed* evolves the two *ions*, chlorine and lead, the former being an *anion* and the latter a *cation*.

"These terms being once defined, will, I hope, in their use enable me to avoid much periphrasis and ambiguity of expression. I do not mean to press them into service more frequently than will be required, for I am fully aware that names are one thing and science another."

Names indeed are one thing and science another, as Faraday says. The chemist is concerned with solutions and there is reason to believe that electrolytic conductivity is confined to the liquid state. Faraday made no assumption of ionic freedom and the question ever at issue, these forty odd years past, has been: "What are the ions, what is their state, *in a solution*?" One or the other party must give up the use of the word and coin a

new term. The matter is of consequence, as chemistr is at root an electrolytic science, chemical change bein demonstrably an affair of current electricity; this wa made clear by Faraday all but a century ago. W worship his memory but pay heed neither to his finding nor to his philosophy. Galvani and Volta laid th foundations of chemical science on its active side—ye no chemical student is made properly alive to the natur of the service they rendered; still less is he fully groundec in voltaic electricity. The subject is also neglected b the physicist, who to-day lives only upon electricity o electro-magnetic origin. It is true he uses the Faure cel as a transformer but without thinking what it transform or how it transforms. Work on electrical conduction ir gases is carried out without the slightest regard to th chemical conditions underlying the phenomena—th result being that we are in a welter of uncertainty as tc what really happens. And we rate ourselves "scientific."

My third contribution to the *Encyclopædia* was to th twelfth supplementary edition, published in 1922; i covered pages 621 to 658 and was definitely written tc bring the subject up to date.

Much was said of the advance in our knowledge of th "elements" and of the manner in which we were at las able not only to classify them in exact serial order bu also to indicate where they were missing; it is an interesting fact that, in the interval, owing to the indication afforded of the nature of the missing elements, it ha been possible to institute a direct search for these and apparently, we are upon all their tracks. Up to and including Uranium, ninety-two distinct types are now recognised but a number of these exist in several homologous varieties.

The table on pp. 24, 25 is a complete list up to the date

of publication. The number prefixed to the symbol of each elementary species is its serial number. That following the symbol is the number hitherto known as the atomic weight applicable to the material which we can directly handle. In the case of a mixture of homologous species (isotopes), this is a net value and not the individual atomic value. When the element exists as a single species, o is placed below the symbol; in dealing with those of which "varieties" exist, the masses of the several homologues (and therefore their number) are given in an order which indicates their relative abundance. Thus, in the ordinary material, chlorine is a mixture of two homologous species, whose relative masses are as 35 : 37, the former predominating. Thus far, two homologues have been met with apart only in one instance—that of lead. Excepting hydrogen, the atomic masses of individual species are all practically whole numbers; no number is met with twice over in two families. The similarity in the relationships between the various elements thus arranged with those existing between homologous and isologous hydrocarbons is very striking.

The table is of profound significance. The vast mass of exact work by a long line of heroes that is embodied in it defies description. To have lived through the period of such achievement and mark its fruition is to have lived indeed. It can be read with full understanding only by those who are fully versed in the facts behind it and have the great scheme of organic chemistry vividly in mind.

Mere elements, however, are in danger of being relegated to the past. Knowing nothing really of what is happening upon earth, we are beginning to dream of chemical conditions and happenings in the stars, where the temperatures are so transcendental that the atomic nuclei, the protons, so we are told, not only cast off their

light electronic clothing but, as a consequence, all the whalebone that kept them at respectful distances apart being destroyed, as they are subject to enormous pressure, are forced to forget that they were once kinetic units and are pushed closely together, like lion and lamb, so that the thoroughfares become crowded and packed to a density beyond belief. Even then the poor naked things are not safe—at temperatures estimated at only hundreds of millions of degrees, a " radiation " generated within them, how, when and where, we must not inquire too closely, comes into operation, whereby matter is annihilated, flashing into energy of radiation : thus immaterialised, the star just hits out into space. What this change is worth may be apparent when it is stated, " that whereas the ordinary combustion of a ton of coal provides energy enough to drive an express train for an hour, the annihilation of a ton of coal would provide enough energy for all the heating, lighting, power and transport in Great Britain for a century." Coal, however, is never to reach this value on our earth.

The stellar atoms to which these things happen, we are told, are those of " elements " more complex than uranium, present in young stars. The atoms in a star becomes simpler with its age. Evolution appears to be from complex to simple. In chemistry, this is true of simpler compounds but not of hydrocarbons, the complexity of which increases up to that of " char " as the temperature is raised—still, carbon is carbon. Our terrestrial elements are said to have so little capacity for spontaneous transformation that they may properly be described as permanent. This is comforting—uranium does not seriously count in ordinary life and we may let that go. If, however, our elementary store be so absolutely proof against superthermal attack, it seems to be a little difficult to grant Rutherford's claim to have shot

hydrogen spots off simple nitrogen atoms by means of mere helium bullets.

Who shall say that there is no poetry in science—that the astro-chemist and physicist is not worthy to appear in the Chicago Wheat Pit? He is certainly a bold speculator in "futures." Still, investments have to be watched. All this is to be read in *Nature* of December 4, 1926.

Writers with such romance at the points of their pens should easily outdistance those whose imagination is sheltered under Green Hats or bounded by Spoons. If so much can be made out of the elements by imagination, they should be attractive objects of study even to the lay reader—the more as some of them are the bricks and mortar of which he is built.

To return to the cold, tame conditions of our earth, in my third article in the *Encyclopædia* I referred at some length to the growth in our knowledge of solid structure owing to the introduction of the X-ray method of analysis and to the development of geometrical methods of correlating crystalline form with structure, specially considering the work of Sir William Bragg and his school on the one hand and that of Mr. William Barlow on the other. I also hinted at the effect upon our views of molecular structure which the introduction of conceptions derived from a solid geometrical treatment might have.

In the interval, progress has been less rapid than was perhaps expected. It is clear that the problems before the X-ray analyst are complex and very difficult. Here, again, the co-operation between physicist and chemist has not been the close one that is essential to success. In not a few cases the solutions offered are absurd—such as no thinking chemist can accept. Particularly is this true of the contention that in a salt like sodium chloride

the atoms are all "ionised"—that is to say, they enjoy a free, independent existence and are not present in combination as molecules containing both elements.

The solution, moreover, is not in accordance with the crystallographic peculiarities of such halides.* A simple geometrical solution of the problem has been advanced by Mr. Barlow, which is compatible with the assumption that there are definite molecules of sodium chloride in salt. Unfortunately, X-ray workers have adopted loose methods which admit of almost any interpretation. Until we have models indicating something more than mere centres of absorption, we shall have difficulty in translating their conclusions into practical terms of structure.

In discussing the progress made in the study of the processes of chemical change, I dwelt more particularly upon the effects produced by enzymes, the strange, selective agents which dominate the life-process in animals and plants. In the interval, some progress has been made in purifying and thereby greatly enhancing the activity of several of these; we are no further advanced, however, in our knowledge of their exact nature.

A captious critic of one of my articles complained that I had expressed my own views—too freely—instead of

* Since this was written, an account has been given, in the *Zeitschrift für Krystallographie* (1926, p. 265), of observations on the etch-figures formed on a surface of crystals of potassium chloride, which tends to show that the lack of symmetry sometimes observed in these halides may be an effect produced by the presence particularly of an organic impurity. Assuming, however, that they be strictly cubical, there is no reason to suppose that they may not consist of interconnected molecular units. If the centres in the cubic point lattice be enlarged equally until they meet as spheres, although each sodium unit may appear to be surrounded by six chlorine units and each chlorine unit by six sodium units, several chlorine units are also in touch. It is possible to think of a chlorine unit as in combination with only a single sodium unit and yet as united to several chlorine units and the chlorine units as forming a network extending throughout the mass. The mass in such event might be the molecular unit and no unit within it individually active.

giving the opinions of others. It is the only evidence I have had that such articles are looked at, except that, on one occasion, a librarian called my attention to a misprint. I am inclined to Mr. Huxley's opinion "that one does not oneself go mad in the process of reading the *Encyclopædia*, a mine of useless and uncorrelated knowledge, is due to the fact that one forgets." Whatever effect my diatribes may have produced upon readers, they are forgotten. The book is probably one that is not used by students, especially in these days of examinations. It is a great work of reference, mainly for libraries, to be put upon the shelves of those few who are prepared to follow Mr. Huxley's good example and improve upon it by using the volumes in their waking moments, not as a soporific.

When asked to bring my article in the twelfth edition up to date and at the same time shorten it, I urged the editors to allow me to write the article in a manner to bring the subject more within the compass of the general reader—the real users of the work—and so that it might serve to interest the junior student, the senior schoolboy, in fact, even the teacher. I was fortunate, through Dr. Hodgson's kind offices, in obtaining the desired permission and would here give my grateful thanks to those concerned, especially for permission to republish the article in book form.

The first of the essays in this book is the article in question, as it appears in the thirteenth edition of the *Encyclopædia* published in September, 1926. The earlier part is written to give a general idea of the subject, in so far as this was possible in the brief space at my disposal; in the later parts I have perhaps aimed higher and endeavoured to deal with matters of special interest, particularly to the biologist, including the medical man. In the original, there were not a few cross references to

other articles in the *Encyclopædia*, on topics which would ordinarily come under discussion in a chemical primer; hence some blanks will be apparent.

Unlike Mr. Wells, I make no claim that my book is a novel. On the contrary, it deals with old matter but matter which must have eternal youth in the student's eyes.

The second essay is a lecture delivered before the Society of Chemical Industry, reprinted from the Journal of the Society, 1923, Vol. 41, 253-270. Then follow three essays which were originally published in *Science Progress*. Finally comes a paper taken from the Proceedings of the Royal Society. I am indebted to all these sources. All are arguments for the interpretation of chemical change upon lines laid down by Faraday. Water especially, which is always neglected, is made much of and the part it plays and its complexities are evaluated as far as possible.

There are signs that sanity may ere long prevail. In the article surveying Physical Chemistry in the recently published *Golden Jubilee* number of the Journal of the *American Chemical Society*, Wilder D. Bancroft points out various shortcomings in current theory and even goes so far as to say that:

> "Forty years of intensive development have brought us to the point where we cannot determine any electrolytic dissociation with any degree of accuracy and where we question the significance of the term 'electrolytic dissociation.'"

His most striking admission is the following:

> "It is easy enough to point to one factor which has been neglected practically completely and which may be the one which has caused most—and perhaps all—

of our difficulties. For years H. E. Armstrong in England has chided the physical chemists for considering water only as water, whereas it is a complex and variable mixture. This criticism seems well founded . . . there is no reason for despondency about the electrolytic dissociation theory and about concentrated solutions until after we have determined the effect of the changing polymerisation of water on our formulas; and by that time there may be no cause for despondency."

No better indication, that "we don't know where we are" could well be given. To me, at last, such revenge comes as sweet.

Again, in *Smith's Inorganic Chemistry*, revised and rewritten by James Kendall (1926), a book full of most valuable information but also of delightful contradictions, water is at first lightly spoken of in the following terms (p. 135):

"All the 'dilute' acids contain 70 to 80 per cent. of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned and is therefore omitted from the condensed statements of their reactions."

Recantation comes, however, on p. 394:

"*The Part played by the Solvent in Ionisation.*—So far, we have regarded water as playing merely a physical rôle in the ionisation of electrolytes. The ions in a solution of hydrogen chloride, for example, have been regarded as H and Cl, the solvent breaking up the molecule HCl in some way but not being itself directly concerned in the reaction. This view, although sufficient for many purposes, will not stand strict investigation. . . . In one important class of ionic reactions, nevertheless, namely those which represent *hydrolysis* (*the* interaction conditioned by acids!), the water must be

taken into careful consideration, as we shall discuss in detail in a later chapter. Recent work, indeed, suggests that the distinction drawn between solvent and solute in explaining ionisation phenomena is entirely misleading. Pure liquefied hydrogen chloride is practically a non-conductor just like pure water. It is quite an arbitrary procedure, therefore, to ascribe all of the conducting power of a mixture of hydrogen chloride and water to the former substance and to regard the latter as quite inert. It would be more logical to consider both components of the solution as equally concerned in ionisation."

The interaction of two such simples as the molecules HCl and H_2O is nowhere considered. I may also point out that, whereas, in Smith's book, all the specious "Bulls" airing Ionic speculations are fulsomely quoted and even "illustrated," those few of us who have been "Bears" of this stock from the beginning are never mentioned. I care nothing for priority—yet it is interesting to have proof, even in a text-book, that the literature has been considered and there are conventions to be observed even in the society of the scientific world; some day, it will be possible, perhaps, to speak of this as "polite."

Even a worm will turn. I am still of too active a disposition to be satisfied with the calm seclusion afforded by the *Encyclopædia Britannica* or by so reputable a body as the Royal Society. Having no Ostwald, I must act as my own trumpeter. I am seeking a hearing for interpretations which were advanced before Arrhenius was recognised, developed without the slightest knowledge of his speculations, brought before the Chemical Society and the British Association in 1885, the Royal Society in 1886 and often amplified in the interval. I ask less for consideration of what I say than for an interpretation

of work of the high importance of that done especially by H. B. Dixon, H. B. Baker and William Bone in its bearing upon Faraday's doctrine of the essential identity of chemical and electrolytic change. My desire is to see chemistry made a rational study and an intellectual discipline—not a mere catalogue of facts and formulae, nor the subject of spurious mathematical deductions.

Chemical theory, to-day, is in a most destitute condition, a disgrace to our cloth, in no way congruent with our vast knowledge of fact: far too many chemists are working in alleys and backwaters, without proper guidance or the possibility of appealing to reason. The state is one to be remedied without delay, so that the fascinations and grandeur of our science may be apparent, its infinite and fundamental value fully realised.

H. E. A.

January, 1927

THE ART AND PRINCIPLES OF CHEMISTRY

CHEMISTRY is the study of the components of the universe, of its ultimate materials, a branch of natural science. In ordinary life, we judge of man's character from his actions: so also in chemistry. The science had its beginning when man became a living soul and not only began to see and compare the objects about him and to notice changes but also to make logical constructive use of his observations.

Fire, in the form of the sun, must have been his first wonder but the fear of fire will have come upon him by accident, we may suppose—if not from the volcano, in the thunderstorm. His appreciation of its value will have varied with the conditions under which he lived, whether in a cold or a hot climate. The north American continent is without fire, though at times visited by devastating electric displays. England is not far from mounts Vesuvius and Etna and close to Iceland, one of the great volcanic regions of the world, though a region of ice and snow. The English owe much to their Scandinavian ancestry and as Carlyle has told us, the primary character of the old Northland mythology was "the impersonation of the visible workings of Nature. Earnest, simple recognition of the workings of physical Nature, as a thing wholly miraculous, stupendous and divine. What we now lecture of as 'Science' they wondered at and fell down in awe before as Religion." Our task to-day is not only to recover this attitude but to put aside mythology

and elevate our science into a pure religion—the use and pursuit of truth.

Discovery of Fire

Sooner or later, man will have sought to make fire for himself. The most primitive method is by friction—by forcibly twisting a stick backward and forward in a hole in another piece of dry wood or by rasping one piece rapidly across another. This method may conceivably have been discovered in drilling holes into stones—in making hammer heads—or through pieces of bone, etc. Women early wore necklaces of rude beads and perhaps began by threading berries or flowers upon grass stems or rushes, as children do to-day, so discovering the decorative effect of colour. That red-ochre was used to decorate the body from an early period is clear, from its constant occurrence among the remains of primitive man. The production of fire by friction, however, must have entailed a vast exercise of thought—as the heat that is generated has to be applied in raising easily inflammable material to the burning point. A second primitive method was to catch the sparks produced on striking the mineral *pyrite* with a piece of stone. Modern travellers have found this method in use among the Esquimaux, who autually mine the material for the purpose. We know this method came before the use of flint and steel, as pieces of the mineral have been found in the earliest cave-dwellings, along with the most primitive flint implements: the latter method, necessarily, did not arise until the discovery and use of iron—itself one of the marvels of early human inventive power.

Discovery of Lime

Thunder, as Carlyle tells us, to our Northland ancestors, was not mere electricity, as it is to us—it was the God

Donner or Thor, God also of beneficent summer heat. Savages, when they have first seen fire, have thought it to be a devil or God that bit you sharply when you touched it and that lived upon dry wood. Familiar as we are with it to-day, we use it more often than not without a thought of its meaning; indeed the nature of fire has been but slowly disclosed to man, although its effects have long been obvious. Some of these, we can easily picture. In England and throughout Europe, wherever possible, primitive man has lived in limestone caves and excavations. One of the most inhabited parts of the island was the south-eastern district where the soft limestone, chalk, prevails—in this region, indications of early human occupation are everywhere present. Living in such caves, man will often have built his fire surrounded by blocks of chalk, as we do to-day, using any stones at hand, if we wish to boil our kettle in the open.

The harmless, unobtrusive limestone will thus have been burnt (calcined) and necessarily, from time to time, lumps will have been cast out from the cave and wetted by rain. Some observant person will have noticed that, when thus wetted, the lumps have burst asunder and grown hot, even giving off steam, whilst falling into the finest powder. Thus for all time, the easy method of reducing limestone into powder will have been discovered. Sooner or later, also, the greater growth of grass in places where the powder had been spread about will have been noticed and the use begun of lime and limestone as an agricultural fertiliser. Children playing with the wet lime must have felt its caustic effect, and spilling it upon their skin clothes will also have found out its hair-removing power: hence its use by the tanner. A distinction will thereafter have been made between mild (unburnt) and caustic (burnt) lime. Many such "simple" discoveries will have been made, in course of time.

Other stones will have been collected and burnt, just

to see what happened. Being burnt in contact with charcoal, metallic ores will have been reduced and thus metals discovered, such as tin, copper and eventually iron. Tin and copper often occur together and their ores are very easily reduced—so it came, probably, that bronze was the first metal made, though we may suppose that the concept metal was first excited in the mind of man by gold, which occurs native.

An Experimental Science

Chemistry, above all others, is *the* experimental science. The science began when wise men advisedly made experiments—apparently either with the object of discovering ways of transmuting metals into gold or of finding remedies for sickness, if not of lengthening life. We can almost restore the course of action followed. *Pyrite*, being of household value, will have been collected and stored. When stored, under ordinary conditions, especially if exposed to moist air or rain, it gradually "decays," changing to a soft brown solid, like the rust which so easily collects upon iron that early man must have known well. As when pyrite is burnt a pungent smell is obvious, like that from burning sulphur—a substance well known from its occurrence in volcanic districts—glimmerings of the presence of both iron and sulphur in the mineral will have been excited in observant minds and the foundation laid of modern methods of qualitative analysis. Stored in the open, the heaps of decayed pyrite will often have been washed with rain: here and there the washings may have been collected in pools and when these dried up, in fine weather, green glass-like crystals of *green vitriol* will have been deposited. Glass-like substances generally were distinguished as *vitriols* by the early workers. They tested everything with fire, so "distilled" this vitriol and thus discovered *oil of vitriol*; later on this was made by burning sulphur

under special conditions. The name oil of vitriol is still popular, though *sulphuric acid* is that now given to the liquid because of its connection with sulphur. No doubt, the discovery was very soon made that oil of vitriol or *vitriolic acid* was an extraordinarily corrosive substance and its effect upon substances generally was therefore studied. When added to common salt, it expelled a vapour or spirit—*spirit of salt*—which was very soluble in water. To the present day, the solution is sold as *spirit of salt* or *muriatic acid*, because of its preparation from salt (*murium*). Vitriolic acid was also found to act upon nitre, again a natural product often met with near to human habitations, giving rise to a very volatile, corrosive liquid, which dissolved nearly all the metals—hence the name *aquafortis*, still in use among jewellers, which later gave place to *nitric acid*. Thus were foundations laid.

An Exact Science

Chemistry came to rank as an exact science with the introduction of the balance. The first *systematic* inquiry involving the use of the balance was that of Joseph Black, in 1755, into the nature of magnesia alba and limestone. His account is a classic, to be read by everyone who has the slightest desire to understand chemical method—for Black's method is our modern method and it is to him, more than to anyone, that we owe the introduction of the logical quantitative spirit into our subject, though it was not until Lavoisier had made firm the foundations laid by Black that the force of the method was fully recognised and its use became systematised and established.

Let us endeavour, as far as possible, to put ourselves into Black's position. To-day, when cement is so much used in place of lime as a building material and few of us see lime slaked to reduce it to a fine powder before mixing it with sand, we may best open our inquiry by procuring

several lumps of limestone and—if we be unable to make it ourselves—of the lime made by "burning" it and begin by slaking a lump of the lime, laid upon a plate, first weighing the lime. As it is always well to deal with known quantities, we may also take a known amount of water. Tins are at hand everywhere and it is easy to beat out a spout at the edge of a small tin box and to weigh this, say, half-full of water.

Pouring the water over the lime but down a rod—a pencil will do—to prevent spilling, distributing it evenly and allowing it to soak in before adding more, we stop when the lime is visibly wet. Soon, if not at once, the block grows hot, begins to crack and fall to pieces and much steam is given off. The change is marvellous—that cold water should so produce heat is astonishing! What has happened? Is the water all got rid of as steam? On weighing the cold slaked lime, now a fine, dry powder, it appears that from 100 parts of lime and x parts of water, there is produced 100 + y parts of the slaked lime, only x − y parts of the water having been given off as steam. So the lime has, in some way, been joined to water and apparently the heat has been produced as a consequence of the act. *Limestone* never behaves in this way to water—what happens then when it is burnt to lime? What is the effect of burning things? Usually they are more or less completely destroyed. Is the limestone? Experiment shows that, when strongly heated, all limestones lose in weight, some as much as 42–43%. The cleaner the limestone, the more it loses, the best whiting (so-called because it is used in making whitewash), prepared by levigating finely ground chalk, losing the most. Sometimes, in limestone rocks, crystalline masses and even crystals are found of the mineral *calcite*; this also appears in limestone caves in the form of stalactites. When this is burnt, it not only gives lime but more than any other form of limestone. When every possible care is taken to be exact, the amount obtained is constantly—*within the limits of experimental error*—56% by weight

of the calcite: so 44% is in some way lost! Precise determinations of the amount of water taken up by the 56 parts of lime so produced show it to be the merest trifle above 18 parts. What of the 44 that are lost in "burning" the limestone?

Study of Calcite

As calcite is thus found to have a definite composition and seems to be a pure limestone, the term may be used in preference to "limestone," which is the name not of a mineral species but of a rock that is found all over the world. How is it to be tortured into displaying its character? Its actions must be studied in full. As it is deposited as stalactite by the evaporation of water which has drained through limestone rock, the material must be soluble to some extent even in water. Solvents more powerful than water are known—do these affect it? Muriatic and nitric acids dissolve it readily but with effervescence—*i.e.*, gas is given off, *calcite gas*, let us call it provisionally: how much? The experiment being made in an apparatus which can be weighed before and after the escape of the gas, this also being collected and measured, it is found that 100 grammes of calcite afford about 44 grammes of gas and that these 44 grammes of gas measure about 22 litres. The missing 44 is thus caught and shown to be a gas—no wonder that when limestone is burnt nothing is seen to escape. What of lime? Is lime soluble in acid? Experiment shows that it is and that, as was to be expected, it dissolves without effervescence. It is thus made clear, that a gas is imprisoned in limestone which may be expelled by heating and also by means of acid. Hence the name "Fixed Air," used by Black. What is this gas, this fixed air? Is it one of the gases we know? We know *air*—we feel it as wind—though we do not see it. Every one knows vaguely that air is life—that we inhale it and that we are kept warm by its use; it is also known that fire is in some way

promoted by it: that burning involves an interaction of air and the fuel. Some few have learnt that less than 150 years ago the discovery was made, that the active constituent of air is the gas *oxygen*, of which there is nearly 21%, all but about 1% of the remainder, as we now know, being nitrogen, which is inert. To-day, oxygen is produced in large quantities by liquefying air under pressure and separating the oxygen and nitrogen by distillation, just as we separate, for example, alcohol from water or petrol from crude petroleum. To compare these gases with calcite gas, we may ascertain the weights which have the same volume as the 44 parts of this gas obtained from 100 of calcite—the weight of the oxygen is 32, that of the nitrogen 28.

Oxygen

Oxygen being thus easy to get—it is used on the streets from big iron cylinders, into which it has been compressed, in welding iron rails by the oxy-acetylene blowpipe—we may test its behaviour in promoting burning. Anything which burns in the air, if kindled and introduced into oxygen, burns far more easily, often with great brilliance and energy. Wood, charcoal, coal, oils and alcohol all burn but only the flame is conspicuous: there is neither visible nor obvious product. Sulphur, used of old on matches, because it is easily fired, evidently yields a product, judging from the smell that is noticeable. Phosphorus, which burns with particular brilliance, yields a white solid. Why the name *Oxygen*? The terminal *gen* is an indication that it is a generative material. The name was devised by the great Lavoisier—who was decapitated by the French revolutionaries in 1796, because the Republic had no need of savants—to express the fact that common combustibles were converted by it into *acids*, from the Greek *oxys*, acid, *gennao*, to produce. Oxygen remains, to-day, the most significant term in chemistry. Lavoisier's prescience in selecting it was

absolute. The white snow from phosphorus, the fumes from sulphur, dissolved in water, taste acid and turn a vegetable blue colour, such as violet-juice, red ; what of the product from charcoal, if there be one ? On kindling charcoal in a current of oxygen and passing on the gas into a solution of blue litmus, the solution is reddened, though not made red. All vegetable matters, when burnt, together with more or less water, give a similar product, in that it is weakly acid. What of the gas from calcite ? Passed into a solution of litmus, it causes faint reddening : at least a clue to its nature is thus obtained. That it is to be connected with coal or carbon was known at an early date—not only to Black but to his forerunners. Let us now consider how the connection may be established. Calcite, we have seen, is easily resolved into lime and calcite gas.

Can the gas from calcite be reunited with lime to reproduce calcite ? Though but slightly soluble, lime is more soluble than calcite : lime-water has long been used medicinally : so if the lime in lime-water were to associate with the gas, when the two are brought together, the reproduced calcite might become evident by falling out of solution as it was formed. On passing the gas from calcite into lime-water, a white precipitate *is* formed. Having ascertained the solubility of lime, it is easy to prepare enough lime-water and from this make enough of the product to find out whether it can be burnt to lime and, if so, what percentage be lost, also how much gas be set free on dissolving it in acid. The values agree with those obtained with calcite—moreover, seen under the microscope, the crystalline form of the product is like that of calcite. It being thus established that calcite can be reproduced from the two substances into which it is resolved by "burning," lime-water becomes a test for calcite gas. On burning charcoal or other "carbonaceous" material in oxygen and passing the product into lime-water, precipitates are obtained which prove on examination to be *calcite*, being like it in crystalline form

and in composition, 100 parts yielding 56 of lime and 44 of gas. It is thus discovered not only that *carbon* is a constituent of limestone but that calcite gas contains both oxygen and carbon: the proportions in which these are associated are found, by burning known weights of carbon, to be as 12 to 32 in the 44 parts of gas obtained from 100 of calcite. As equal volumes of the gas and of oxygen weigh as 44 : 32, the gas may be said to contain its own volume of oxygen. It is now possible and desirable to use the more significant name *carbonic acid gas*, in place of calcite gas.

Having thus resolved limestone into three components, lime, carbon and oxygen, we may ask, what of lime? What happens when it is attacked by, say, muriatic acid? This latter is a solution of the *spirit of salt* in water—take away the water, which is known to have but a slight solvent effect upon lime, what will be the action of the spirit of salt?

On passing the gas from salt through a tube containing lime, this grows very hot and gradually liquefies; ultimately, with care, a liquid may be distilled off. On examination, this behaves exactly as if it were *muriatic acid*, a solution of the "spirit" *in water*. Apparently, water has been produced from the two interacting materials—what is water? What else is formed? The tube contains a solid, looking much like fused common salt. Is this "muriate," perhaps, common salt! If so, it should behave like salt and give spirit of salt when "tortured" by vitriolic acid. The experiment being tried, spirit of salt is found to be given off—but the residue differs from that obtained on thus treating salt, being but slightly soluble in water. The product from lime and spirit of salt is, in fact, a muriate, a *sea-salt*-like substance—a *haloid*—but not sea-salt. When the "vitriol" from the lime is studied, it is eventually found to be the well-known common mineral *gypsum*, which thus becomes connected with limestone. Clearly, something passes from the spirit of salt to the lime—does the

reverse happen, perhaps? Is it a case of exchange? What is water? What is spirit of salt? Such questions were only recently answered. The compound nature of water was not suspected until towards the close of the eighteenth century. Priestley, in 1781, observed that "inflammable gas," as it was then called (made by dissolving iron, zinc or tin in muriatic acid), gave *dew* when exploded with air. Cavendish, repeating the experiments, came to the conclusion that the dew was plain water and subsequently produced water by exploding inflammable air with oxygen. Even earlier (1776), Macquer, in France, had recognised that water was produced on burning inflammable air. Lavoisier then studied the matter fully and eventually gave the name *hydrogen* (water-producer) to inflammable air. The first step toward proving that spirit of salt was a compound was the accidental discovery of the gas we now call *chlorine*, by Scheele, in 1774, on dissolving a new mineral (manganese) *pyrolusite*, which he was examining, in "marine" or muriatic acid. Gay-Lussac and Thénard subsequently showed (1809) that hydrogen was produced on passing the gas spirit of salt over heated iron and that spirit of salt could be formed by the interaction of equal volumes of hydrogen and chlorine gas (*cf.* T. M. Lowry's *Historical Introduction to Chemistry*).

The Caustic Alkalies.—The production of water from lime and the spirit of salt or hydrogen chloride is, therefore, a proof that lime is an oxide—of what? The nature of the caustic alkalies was scarcely suspected until Davy, at the Royal Institution, in 1807, obtained the metals potassium and sodium from caustic potash and soda, by decomposing them by an electric current. Limestone had long been classed with the common alkalies—soda and potash. Moreover, Lavoisier had conjectured that the alkaline earths (lime and baryta) were compound substances and like metallic oxides. This view was confirmed when Davy prepared calcium from lime (1808). The 56 parts of lime in 100 of calcite are now known to consist

of 16 parts of oxygen and 40 parts of the metal calcium. As no further simplification can be effected by the means at the disposal of chemists, nor even by any mental process, the conclusion has been drawn that oxygen, carbon and calcium are simple materials or elements—within the meaning of the act chemical, the act in which an element is defined as a chemically unresolvable substance, for chemists are ruled by acts. Taking the percentage composition of calcite into account, it is noticeable that the ratio in which oxygen is present in the two oxides is $16:32 = 1:2$, which justifies us in speaking of lime as a *monoxide* (calcium oxide) and of calcite gas as a *dioxide* (carbon dioxide).

A vast amount of labour has been expended in determining the composition of water—the quantity obtainable from 56 parts of lime is 18·016, of which 16 are oxygen and $2 \times 1{\cdot}008$ hydrogen. To produce this amount of water from lime, hydrogen chloride (spirit of salt) must be used in the proportions of 56 of lime to nearly 73 of chloride. The amount of chloride used contains $2 \times 1{\cdot}008$ of hydrogen and 70·92 of chlorine. Calcite, we have already seen, is a substance of unvarying composition.

Such values found an interpretation in the doctrine proclaimed by the Latin Lucretius (99–55 B.C.) in his celebrated poem "On the Nature of Things." The doctrine was borrowed, in the main, from Democritus, a Greek philosopher (*c.* 460–380 B.C.). Lucretius taught that everything was formed of indivisible particles or atoms, eternal and unchangeable; these atoms, "by various combinations, in infinite time, with the void in which they move, formed the universe." The doctrine was resuscitated and developed by John Dalton in 1808; to-day it is the accepted, proved basis of chemistry.

Matter is known to us in the three states of gas, liquid and solid. In the true gas, the particles are practically independent and very far apart, yet, as they are in very rapid motion, the distance they are apart is constantly varied and they often come into collision: they also

constantly come into collision with any object exposed to their blows. Gaseous pressure is due to the impact of the particles upon the surface affected.

There is a temperature—the critical temperature—above which no pressure will cause a gas to liquefy; below this temperature, if a gas be compressed, ultimately its particles are brought sufficiently close together to exert an inherent attractive force—more or less powerful, according to the nature of the gas. The gas then liquefies. When the liquid is sufficiently cooled, it becomes solid and crystalline: the particles then take up certain definite positions.

Avogadro's Theorem

Avogadro, in 1811, was the first to enunciate the view that the similar behaviour of gases, under comparable conditions, is to be explained by the assumption that *equal volumes contain equal numbers of particles*: consequently, the relative weight of the particles or molecules are as the relative weights of equal volumes at the same temperature and pressure; *i.e.*, as the densities of the gases. Taking hydrogen and oxygen, for example, the latter is found to be 15·880 times as heavy as the former. Having acquired a strange affection for the number 16 in connection with oxygen, having so often to deal with oxygen in their analyses, chemists have preferred to retain this number and to raise that of hydrogen to $\frac{16}{15 \cdot 88} = 1 \cdot 008$ although hydrogen is their unit of reference in practically every other respect—being the lightest of known elements. Though oxygen molecules are thus determined to be about 16 times, nitrogen about 14, carbon dioxide about 22 times as heavy as hydrogen molecules, it in no way follows that these are more than the relative masses of the molecules. Reflection shows that Avogadro's theorem has important consequences. If we consider compounds, taking water as the most familiar, the gas obtained by vaporising water (dry steam) is only 9 times as dense as

hydrogen under comparable conditions. We know that of 9 parts of water, one is hydrogen, whilst 8 are oxygen. The oxygen molecule, however, is 16 or 2×8 times as heavy as the hydrogen molecule—so that if there be one particle of oxygen in a molecule of water, there must be two particles of hydrogen. As a matter of fact, we know that when water is formed, by exploding a mixture of hydrogen and oxygen, twice as much hydrogen, by volume, as of oxygen is required—twice as many molecules, therefore, of the one as of the other interact. As the volume is diminished by one-third during the explosion, the number of water molecules formed must be only two-thirds the number of hydrogen and oxygen molecules concerned in their production—some division of both molecules, some new association of their parts, must have been effected. It is thus discovered that the molecules have parts: how many? we may ask. Extending the inquiry to the formation of other compound gases from hydrogen, taking spirit of salt or hydrogen chloride, this is found to contain hydrogen and chlorine in the proportion of 1·008 : 35·46. The density of the gas, however, is only about $18 = \frac{36}{2}$, compared with that of hydrogen: a value which is but one-half of the minimum value (1·008 + 35·46) that can be assigned to the amount of the compound containing unit weight of hydrogen. Interaction of hydrogen and chlorine gases to form hydrogen chloride, moreover, takes place between equal volumes, without change of volume. Therefore, the two molecules must be supposed to have been each divided into two, one-half of the one going to one-half of the other: each molecule is a similar composite, the product being a dissimilar composite. It is as if a couple, say, two lively boys, dancing in a ball-room, were to meet a dissimilar similar couple, say, two sedate girls and the two couples exchanged partners: there would still be two couples dancing, their joint effect in the room in occupying the floor would be the same as that of the

original two couples, though they might be less agile than the one of these and more agile than the other.

Chemists have chosen to term the ultimate constituents of molecules atoms. The chemist to-day invariably applies the term molecule to the kinetic unit—the dancing "couple," the term atom being reserved for the ultimate chemical unit. Physicists, thus far, have not made up their minds to use the terms consistently. The atoms, as in the case of mercury, for example, sometimes elect to dance alone, as molecules : molecules are not necessarily complex units. Emphasis may also well be laid here upon the fact, that the *molecular weight* of any uniform substance, in the gaseous state, relatively to that of hydrogen, is arrived at very simply, hydrogen being taken as the unit of gaseous density, *by doubling the value of the gaseous relative-density.* Moreover, representing the hydrogen molecule as H_2, as 2 grammes of hydrogen occupy 22·32 litres at 0° and 760 mm. pressure, the gramme-molecular proportion (the molecular weight in grammes) will occupy 22·32 litres. Equations written in terms of molecules can, therefore, be at once read in gaseous volumes, as well as in mass proportions.

Symbols

The entire system of atomic weights and of chemical formulae rests upon the foundations afforded by Avogadro's theorem. Each element is indicated by a special symbol, wherever possible the initial letter of its name—as H, Hydrogen, C, Carbon, O, Oxygen, Cl, Chlorine, Ca, Calcium. This symbol represents an atomic proportion and with it is always associated a certain numerical value—the atomic weight, *i.e.*, the smallest proportional weight known to be present in any molecule of the compound hydrogen being given unit value, thus—

Hydrogen . .	H = 1·008	Chlorine . .	Cl = 35·46
Carbon . .	C = 12	Sulphur . .	S = 32
Nitrogen . .	N = 14	Calcium . .	Ca = 40
Oxygen . .	O = 16		

Properties of Elements

The properties of an element are not to be defined in terms of any one set of measured values but from its behaviour generally—in fact, the portrait of an element is a great composite into which much must be read that cannot be expressed in exact terms. Chemistry is an art as well as a science and, as in all walks of life, few of its adherents have the artistic sense sufficiently developed to be able to appreciate fully the works that may be set out before them. To give an example. We deduce the properties of the element oxygen, not from the gas as we know it—which indeed is itself an oxygen compound, O_2—but from the behaviour of this and all other oxygen compounds. We probably come far nearer in water and in ozone to what would be the behaviour of *oxygen-stuff* if it were alone than we do in that of the gas oxygen upon which we live. It were far better if we had distinct names for each of the stuffs we think of as an element and for the compounds which their atoms form with themselves. We are told that the diamond consists of carbon but the picture the chemist has in mind of atomic carbon (carbon-stuff) is as far removed from diamond as any two pictures possibly could be. No elemental name could be more appropriate than that of *azote*, given by Lavoisier to the inert gas in our atmosphere—no name better for the stuff of which it is composed, one of the most active known, we have reason to believe, than that he had in mind, though unfortunately he did not know enough to justify him in proposing its use: *aminogen*. Ordinary oxygen gas were far better spoken of as *zote*—unfortunately the name lacks palatefulness. Chlorine is a particularly fit name for the gas we so call; the name chlorhalogen (green salt-forming) would be more suit-

able for the atomic component of its molecules were it not that it lacks euphony.

Diverse Properties of the Elements

Some of the elements are gases, very few are liquids, most are solids. Some, the majority, are *metals*—a term that needs no special explanation; some are very different from metals, *non-metals*; some show a half-way behaviour, whilst looking like metals—these are called *metalloids*. In all about 90 are known. It is claimed that only 92 sorts are possible. The elements are not only thus divisible into three types but into families. The members of human families tend to be more or less alike in their general conduct—though very different maybe in some particulars; indeed we class animals and plants in families because of resemblances—what is more, we think of the members of a family as genetically related. The lion, the tiger, the leopard, the domestic cat are all cat-like, we call them all *felidae*. Hydrogen stands alone in the esteem of chemists—it is Jove: they have made it their unit of adoration, they measure the loves of other atoms by comparing them with the hydrogen atom. Oxygen, however, is the most potent of all the elements: its character is the most marked, it is the most full of energy and shows the widest range of affection for other elements—few decline to be associated with it: it compels all the active non-metals, except fluorine, to join with it in forming acidic compounds; it marries with all the metals to form compounds which neutralise the acids, alkylic (alkaline) oxides—though if the metals be allowed sufficiently to satisfy their polygamic tendencies towards oxygen, they are in the end overcome by it and the outcome of the union is acidic: it also has particular affection for itself.

The Halogens

As to families, chlorine—the major constituent of common salt—is one of a family of four *halogens* : fluorine, chlorine, bromine and iodine. They are a striking company, in that they are all more or less highly coloured and directly offensive to the nose and animal tissues, being very corrosive and poisonous. Their chief chemical peculiarity is their ability to enter into association with hydrogen, atom for atom, forming the hydrides HF, HCl, HBr, HI. These are all colourless gases, very soluble in water ; though not acids themselves, they form acids when thus dissolved. The halogens form compounds with the metals generally.

The Oxygens

Oxygen is remarkable among the elements as the dominant parent of water. This is commonly represented as a neutral substance and appears so to us, because it is so much a part of ourselves : actually it is the most universally active and potent *of known compounds.* With it are to be associated, as members of its family, though somewhat distant relatives in many of their characters, the elements sulphur, selenium and tellurium. These all form hydrides characterised by powerful odours, analogous to *Hydrone*, OH_2, the unit-molecule of water, in composition ; they also form a series of corresponding acidic oxides, SO_2, SO_3, etc. They combine with the metals generally.

Aminogens

Lavoisier hesitated whether he should not give the alternative name *Nitrogen* to the chief constituent of air.

In selecting *azote*—a name which the French have logically preferred to the present day—he recognised the peculiarity which renders it of value as a diluent in our atmosphere. Recognising the remarkable properties of *ammonia*, he was inclined to use the term *aminogen* but was eventually led to select nitrogen, because of the relation of the element to nitre and nitric acid. At that time, little was known of the great part played by nitrogen in nature and of the existence of ammonoids derived from other elements. Nitrogen is to be associated with the elements phosphorus, arsenic and antimony, because these all form hydrides like ammonia, NH_3; they also form acidic oxides and acids like those formed from nitrogen.

Carbon

is a host in itself, the most wonderful of all elements in giving rise to a vast number and variety of compounds, all of which may be regarded as built upon the single simple foundation stone afforded by its lowest hydride, CH_4, *methane* or marsh gas. It is usual to associate it with silicon and titanium, particularly because of the analogy in the empirical composition of the oxides; the relationship is a distant one, however. Methane is an entirely neutral substance.

Metals

The non-metals are distinguished, speaking generally, by the formation of simple gaseous hydrides. The metals are not to be thus characterised, though hydrides of many are known. They are to be recognised rather by their behaviour towards acids, from which they displace hydrogen, forming salts; also by combining with chlorine and with oxygen in characteristic proportions.

Several families are to be distinguished. The sodium family containing lithium (7), sodium (23), potassium (39), rubidium (85·4) and cæsium (132·8), is characterised by the fact, that they are all soft metals which act vigorously upon water, liberating hydrogen and forming hydroxides, such as caustic soda ($NaOH$) and its analogues. They all unite with the halogens, forming halides or haloids similar to common salt, $NaCl$.

The metals of the calcium family, calcium, Ca, strontium, Sr, barium, Ba, are also soft and readily attack water, forming hydroxides resembling "caustic lime," $Ca(OH_2)$, and combining with the halogens to form dichlorides, $CaCl_2$, etc.

In fine, if the symbols of the elements generally be written in a continuous series, in the order of their atomic weights, it is obvious that throughout the series there is a progressive alteration in properties, accompanied by a periodic rise and fall, certain properties reappearing at intervals throughout the series. This peculiar relationship was specially insisted upon by the Russian chemist Mendeléeff and is commonly referred to as Mendeléeff's periodic classification. This periodicity comes out most strikingly when the volumes calculated as occupied by atomic proportions are contrasted with the atomic weights and also when comparison is made of the variation in the heat-capacities of the elements cooled to the boiling point of hydrogen (− 253°), as in the diagram opposite.

Radium

Chemists, especially those who are conversant with the manner in which function is correlated with structure in carbon compounds, could not fail to be struck by these relationships. They have, therefore, long held the belief that ultimately the supposed elements would be found to

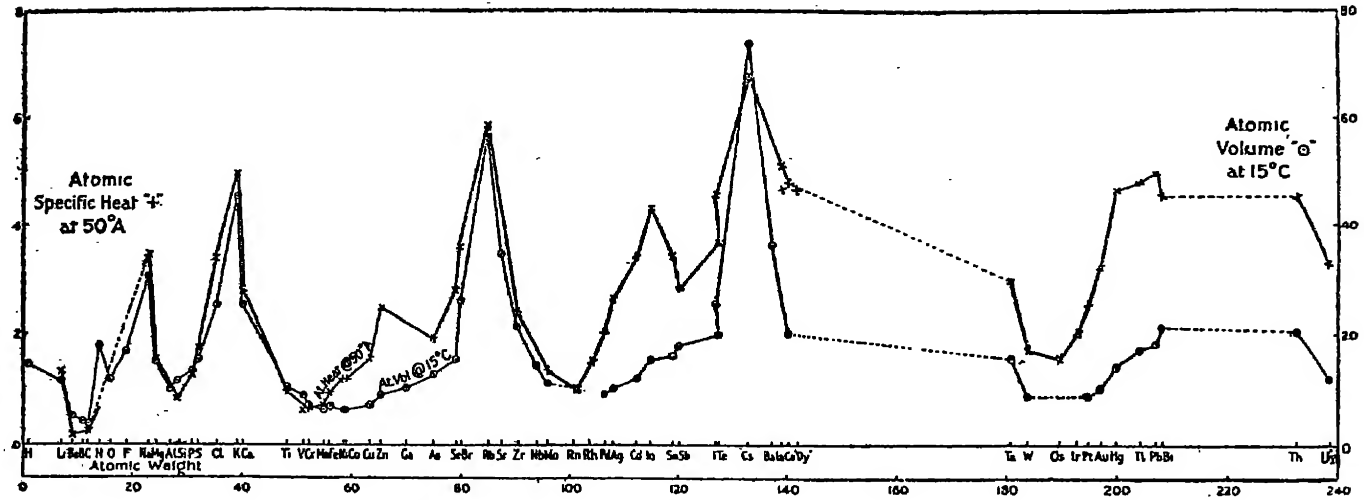

Atomic
Specific Heat "+"
at 50°A
Atomic
Volume "⊙"
at 15°C
At. Heat @ 50°A
At. Vol @ 15°C
Atomic Weight

FIG. I

be composites that were in some way structurally related. The discovery of *radium*, in 1903, suddenly gave substance to this view and the modern electronic conception of the structure of matter is no more nor less than its justification. At present, radium is the riddle of our chemical universe. To all appearance an element, in that it closely resembles the metal barium, it differs from all that were previously known, except thorium and uranium, in that it spontaneously undergoes decomposition, at a definite rate, giving rise to helium and another gas (radon), the which gas, in turn, again gives off helium and is ultimately converted into lead. Strangely enough, we cannot influence these changes by any of the means at our disposal. Whatever lead may be, radium and the intermediate elements seem to be its helides. Helium is suddenly become to the chemist one of the most interesting of known substances.

Isotopes

Ballistics have played a great part in the further recent development of our knowledge. The molecules in gases are always in turbulent motion. First Sir J. J. Thomson, then F. W. Aston, have developed methods of firing atomic molecules (molecules reduced to their ultimate degree of fineness) through a very narrow tube and directing their course of travel by electric and magnetic controls, so that they are delivered at a photographic plate at points determined by their mass and the electric charge they carry. From the photographs so obtained, it is possible to deduce the masses of the impinging particles. Treating nitrogen and oxygen in this way, hits are scored in positions 14 and 16—showing that the ordinary diatomic molecules of the gases are resolved into monatomic molecules. Hydrogen hits are scored slightly off

position 1, in agreement with the conclusion that it is slightly heavier than unity.

The strangely fractional atomic weight of chlorine, 35·46, has always puzzled chemists: some have even thought that the gas was a mixture. Aston has shown that this is so. Firing the molecules at his photographic plate, he has scored hits at two points, 35 and 37, the impression produced at 35 being about double as intense as that at 37, justifying the assumption that ordinary chlorine is a mixture in the proportion of 2:1 of two sets of molecules, one of mass 35, the other of mass 37. These two constituents of chlorine, apart from the difference in atomic mass, differ so little in chemical behaviour, that they pass as alike: they are like "identical twins" born at slight intervals apart. Such are termed *isotopes*. Isotopes are homologous elements.

Classification of Elements

Chemists are still further indebted to physicists for the aid they have recently received from them in classifying the elementary series and "fixing" their possible number. When a slit of light falls upon a plate upon which fine lines have been ruled close together (a diffraction grating) the slit is spread out into a coloured band or spectrum. In like manner, when X-rays fall upon a crystal surface, striking the atomic centres, which may be regarded as forming lines corresponding to those on a grating, they are deflected to an extent depending upon the atomic masses. When the X-ray spectra of the elements are arranged in the order of the atomic weights, one below the other, they form a stepped series. The staircase is seen to be complete, except in very few places—the number of steps indicated from hydrogen to uranium being 92. In the table on pp. 24–5 the elements are

1. H 1·008

2. He 4	3. Li 6·94 7, 6	4. Be 9·02 0	5. B 10·82 11, 10
10. Ne 20·2 [20, 22]	11. Na 22·997 0	12. Mg 24·32 [24, 25, 26]	13. Al 26·97 0
18. A 39·91 [40, 36]	19. K 39·096 [39, 41]	20. Ca 40·07 [40, 44]	21. Sc 45·10 0
	29. Cu 63·57 [63, 65]	30. Zn 65·38 [64, 66, 68, 70]	31. Ga 69·72 [69, 71]
36. Kr 82·9 [84, 86, 82, 83, 80, 78]	37. Rb 85·44 [85, 87]	38. Sr 87·63 [88, 86]	39. Y 88·9
	47. Ag 107·88 [107, 109]	48. Cd 112·41 [114, 112, 110, 113, 111, 116]	49. In 114·8 0
54. Xe 130·2 [129, 132, 131, 134, 136, 128, 130, (126), (124)]	55. Cs 132·81	56. Ba 137·37	57. La 138·90 0 58. Ce 140·25 [140, 142] 59. Pr 140·92 0 60. Nd 144·27 [142, 144, 146, (145)] 61. Il ? 62. Sa 150·43 63. Eu 152 64. Gd 157·26 65. Tb 159·2 66. Dy 162·5 67. Ho 163·4 68. Er 162·7 69. Tm 169·4 70. Yb 173·6 71. Lu 175·0
	79. Au 197·2	80. Hg 200·61 [202, 200, 199, 198, 201, 204]	81. Tl 204·39
86. Rn 222	87.	88. Ra 225·95	89. Ac 226

1. H 1·008

6. C 12 o	7. N 14·008 o	8. O 16 o	9. F 19 o
14. Si 28·06 [28, 29, 30]	15. P 31·027 o	16. S 32·064 [32, 33, 34]	17. Cl 35·457 [35, 37]
22. Ti 48·1 o	23. V 50·96 o	24. Cr 52·01 o	25. Mn 54·93 26. Fe 55·84 [56, 54] 27. Co 58·94 o 28. Ni 58·69 [58, 60]
32. Ge 72·60 [74, 72, 70]	33. As 74·96 o	34. Se 79·2 [80, 78, 76, 82, 77, 74]	35. Br 79·916 [79, 81]
40. Zr 91 [90, 94, 92, (96)]	41. Nb 93·1	42. Mo 96	43. 44. Ru 101·7 45. Rh 102·91 46. Pd 106·7
50. Sn 118·7 [120, 118, 116, 124, 119, 117, 122, (121)]	51. Sb 121·77 [121, 123]	52. Te 127·5 [128, 130, 126]	53. I 126·932 o
72. Hf 180	73. Ta 181·5	74. W 184	75. 76. Os 190·8 77. Ir 193·1 78. Pt 195·23
82. Pb 207·21 206·06, 208	83. Bi 209	84. Pl	85.
90. Th 232·15	91.	92. U 238·17	

arranged in the order of their atomic weights horizontally and vertically in great families. As in human families, there may be marked diversity of character within a family (see Introduction).

Electro-chemical Relationship

Having thus sketched, in barest outline, the manner in which chemists have gradually developed their knowledge of the materials open to study and established an atomic theory of the constitution of matter, of which an extension is foreshadowed in the electronic conception of atomic matter, we may pass on to consider the value of the several pieces on the chemist's chessboard and the manner in which the game of chemistry is played in the laboratory and in Nature. Progress has not always been premeditated but has often been the outcome of some happy accident to a shrewd observer. Such was the case when Galvani (1779) noticed that a frog's leg was caused to twitch when pieces of two different metals touching at the one end were placed, some distance apart, upon the bared muscles : hence arose the discovery of what became known as the Galvanic current. Soon afterwards (1780), Volta constructed his electric pile, consisting of alternate discs of copper and zinc separated by discs of paper moistened with a solution of salt. Workers were thus provided with a means of producing an electric current. Good use was soon made of it, especially by Sir Humphry Davy. His successor, Faraday, was the first to show, though not until 1833, that the electricity of Volta's pile was identical with that produced by friction or let loose in the thunderstorm. The difference was only in concentration or potential. Frictional electricity, though small in quantity, is of high potential—able to leap across considerable spaces—whilst that from the Voltaic pile

or Galvanic battery (both terms were long in use together) is of low intensity but of any desired quantity. Prior to Faraday, in 1801, Nicholson and Carlisle had passed the electric discharge through impure water, obtaining hydrogen and oxygen; Davy, in 1807–8, obtained the alkali and alkaline-earth metals by similar means.

Electrolysis

Faraday, from 1834 onwards, systematically studied, in an exact manner, the effect of electric currents upon compound substances generally. Some, relatively few, carried or conducted the current and, *as a consequence*, were decomposed. He established two classes of electric conductors—(1) *Metallic conductors*, the metals generally (all *elements*), which carried the current more or less well, conductivity always *diminishing* as the temperature rose; (2) *Electrolytic conductors* (*compounds*) which carried the current but were decomposed *as a consequence*—conductivity *increasing* as the temperature rose. All such compounds belonged to the class of "salts," including acids and alkalies in this class. Apparently, no compound acts as a metallic conductor. The term *electrolysis* was coined by Faraday to express decomposition by an electric current. He termed the compound affected the *electrolyte*. As electrolysis was effected by plunging two platinum plates attached to the two poles of an electric battery into the fused substance or a solution of the substance in water; he termed the plates *electrodes*, the one the *kathode*, the other the *anode*. The two substances into which the salt was immediately resolved were termed *ions*—travellers—one the *kation*, the other the *anion*.

By no means all salts are by themselves electrolytes, in the liquid state. Sodium chloride, silver chloride, lead

chloride and tin dichloride are all easily electrolysed; beryllium chloride, stannic chloride, $SnCl_4$, mercuric chloride, $HgCl_2$, to mention only a few, are not, however. In fact, *per*-salts generally are non-conductors. There is reason to think that only metallic salts are conductors and proof has yet to be given that these would be electrolytes when free from all impurity. The liquid hydrides, apparently, are non-conductors. The conductivity of common water diminishes rapidly as this is purified and is ultimately so slight, that if the impossible were done and all impurity removed we may well suppose that it would be a non-conductor. *There is no other logical conclusion to be drawn from the facts.* Liquefied hydrogen chloride behaves similarly. Yet if the two be mixed, solutions are obtained which conduct readily: the specific conductivity rising rapidly, as the chloride is diluted, to a high maximum, then falling but much less rapidly to nil when water is reached. It seems that two types of electrolyte must be distinguished—(1) simple: certain fluid salts; (2) composite: solutions of salts in water (and a few other media).

Electrolysis is a very definite operation. The substance affected is always split into two equivalent portions or radicles (ions). If a current be passed through a series of solutions, the radicles are separated in equivalent proportions, which are not necessarily atomic. Thus sodium, silver and lead chlorides yield their radicles in the proportions

Cl	Na	Ag	Pb/2
35·46	23	108	103

—Faraday recognised that a definite quantity of electricity was associated with the atom and that the unit quantity (the equivalent) carried the unit electric charge. Much later, Helmholtz insisted on the importance of the

conception of atomic charge and Johnston Stoney termed it an electron. Finally, Sir J. J. Thomson gave precision to the idea, claiming that the electron is, as it were, a material particle of negative electricity, about 1/1800 of the mass of the hydrogen atom. None the less, it seems to be the most masterful unit with which we have to deal. To-day, it is supposed that the atoms consist of highly-condensed, positively charged mass-centres surrounded with electrons, in numbers depending upon the mass of the nucleus.

All such speculation is of infinite interest but, at present, it is outside the chemist's ken; he must await the time when the physicist has developed the subject to the point at which it may be of constructive use to him, particularly in explaining dynamic peculiarities which thus far have met with no feasible interpretation. His own formulae are sufficiently vague and wooden, in their implication. The poor paraphrase those who dabble in electrons would substitute has no real meaning at present. In fact, the time is not yet ripe for the considered use of the electron in chemistry: the substitution of an artifice for a system of proved efficiency, by no means yet exhausted of value, is to be deprecated. At the present day we need more than ever to go back to the laboratory and work seriously and constructively at things we understand and dare speak of truthfully—without pretence of knowledge.

Nature and Conditions of Chemical Change

The electric current "reverses" chemical change but is itself produced by means of chemical interactions—in the voltaic cell. Faraday was the first to recognise the *inseparability* of the two phenomena. No student of chemistry should fail to study his electro-chemical

researches from this point of view. A cheap reprint is published in the *Everyman Series*.

What is a voltaic cell? How does it function? Volta's pile consisted of discs of zinc and copper with an electrolyte (a solution of salt) between them. This has served as the model of all developments of the "cell," which always consists of a metal used as anode, which can be associated with one radicle of the electrolyte, the kathode being an inert metal, usually platinum—or a conducting char (coal). *Three* conductors, therefore, are thus coupled in a circuit: *one* of them, however, is both composite and a conductor. This is the inevitable arrangement of an electrolytic couple or voltaic element. Originally, common zinc was used but this is readily attacked by acid when "uncoupled" and so is used wastefully. Gradually it was discovered that the less impure the zinc the less readily it was attacked when uncoupled: then it was found, that if it were coated with mercury (amalgamated), it was no longer attacked in open circuit.

Notwithstanding this definite statement made by Faraday and his insistence (in 1833) upon the essentially electrolytic character of the change when a metal, like zinc, is attacked by an acid, like sulphuric, practically to the present day, in the text-books generally, little or no heed is taken of his findings. Hydrogen is spoken of as prepared by dissolving zinc in sulphuric acid. Hydrogen and oxygen are said to interact to form water, etc., etc., and bare equations are given as illustrations. The conditions under which such changes take place are rarely, if ever, pointed out and made clear. During the past 50 years, however, a large amount of exact work has been done, particularly by H. B. Baker, which entirely justifies Faraday's statements. It was early observed, by Wanklyn and others, that carefully dried chlorine has little if any action on metals which are readily attacked by the undried

gas. Then H. B. Dixon showed, that a mixture of carbonic oxide and oxygen could not be fired if dry. H. B. Baker extended the observations to charcoal and phosphorus, showing that these did not burn in dried oxygen. On this last occasion (1885), H. E. Armstrong insisted that the conditions required by Faraday's generalisation must be fulfilled, if chemical action were to take place in such cases. Taking the formation of water, as an illustration, he contended that oxygen and hydrogen could not interact, as neither was an electrolyte; further, that interaction would not be induced even by the presence of water, as this was not an electrolyte and did not form one with either oxygen or hydrogen: the presence of impurity (a trace of acid or alkali) was essential to constitute the needed electrolyte. Several years later, this forecast was verified by H. B. Baker and so many similar verifications of the view have been secured that it may now be regarded as an expression of the facts generally. Apparent exceptions have been shown, one by one, to fall out, when proper precautions have been taken to secure the necessary freedom from dirt—defining dirt as matter in the wrong place.

The equation of chemical change may be written generally

$$A_2 + \varepsilon\delta + B_2 = AB + AB + \varepsilon\delta$$

where $\varepsilon\delta$ represents *maybe a mere trace* of the indispensable *electrolytic determinant.*

Catalysts

The term *determinant* should not be confused with that of *catalyst*, which is of frequent occurrence in modern chemical literature. The latter term was first applied by Berzelius not only to the action of sulphuric

acid in promoting the formation of ether from alcohol and of glucose from starch but also to the action of platinum black in promoting the oxidation of alcohol to acetic acid, as well as to the action of the enzyme (ferment) diastase in malt upon starch. These are not comparable changes: the first two occur in solution, the second two at the surface of solids and, as the solid has a specific surface-effect in hastening the change, such actions may be treated apart. It is desirable, in fact, to confine the term catalyst to the solid agent which thus acts, not as mere determinant but in quickening a change already proceeding or which may proceed under the influence of a determinant, the change being one which could not occur in the absence of this latter. The equation of change, when a catalyst (κ) is operative, may be written:

$$A_2 + \varepsilon\delta\kappa + B_2 = AB + AB + \varepsilon\delta\ .$$

Interaction of Acids and Metals

Even when the necessary condition of impurity (the determinant) is secured, no metal can be caused to dissolve in an acid *unless it have a positive heat of dissolution*—or, stated more simply, unless the heat of formation of its oxide be in excess of that of hydrogen. Thus copper is insoluble in acids generally. The approximate heat of formation of copper oxide being only 40,800 or 37,000 units, according as that of cuprous or cupric oxide be taken, that of hydrogen being 68,000 (gramme degree) units—these being the quantities of heat liberated in the use of 16 grammes of oxygen at atmospheric temperature. If, as is contended here, water be concerned at least in most chemical interchanges, this is but a rational result. Though insoluble alone, copper is easily dissolved in presence of oxygen—which acts as an

adjuvant, throwing energy into the circuit—as shown in the following empirical equation :

$$Cu + SO_4 \ldots H_2 + O_2 = CuSO_4 + \ldots + H_2O_2.*$$

The action of copper sulphate in the Daniel cell and of nitric-nitrous acid in the Grove cell is of the same kind :

$$Zn + SO_4 \ldots H_2 + SO_4 \ldots Cu + Cu = ZnSO_4 + \ldots H_2SO_4 + \ldots + CuCu.$$

The Depolariser—Nitric Acid

In a simple zinc-sulphuric acid-copper "couple," the copper plate soon becomes "polarised" by the accumulation of hydrogen. This is prevented by the copper sulphate, as copper is displaced from the salt by the hydrogen and the electrode surface remains uniform ; this displacement, however, involves the liberation of energy, so the compound cell has both a higher electromotive force than the simple cell and gives a steady current. Substances which thus act as *adjuvants* are termed, generally, *depolarisers*. The importance of the limiting effect, imposed by the need of electrolysing water in a circuit of chemical change, has yet to be recognised. Moreover, had simple considerations of this kind and the function of the depolariser been appreciated, the complex series of interactions observed on dissolving metals in more or less impure nitric acid—one of the most involved chapters in chemistry—would have been interpreted without difficulty. It would have been realised that the acid proper acts only in one way—as a compound of the two radicles, H and NO_3. It must be incapable of acting directly as a depolariser. The depolarising action of the impure acid is to be attributed, if not to nitrogen dioxide itself,

* Dots are used here and elsewhere to picture the electrolyte of which the symbols separated by them are the "terminals."

to some nitrous compound which this forms with the acid. The various products, other than the nitrate, obtained on dissolving metals in the acid, are all reduction products, less or more remote, formed by the interaction of hydrogen displaced in the electrolytic circuit in which the nitrous compound acts as depolariser, the rapidity of delivery of the hydrogen determining the extent to which the reduction is carried.

Corrosion of Metals

In recent years, there has been endless discussion over rusting and the corrosion of metals, iron especially. Had the elementary principles of chemical interchange been grasped and taken into account, much of this would have been unnecessary and a more useful direction would have been given to the work. To take only the rusting of iron—this may clearly occur in two ways, either in a simple or in an aided circuit. In so far as the iron itself is concerned, it may be said, without hesitation, that it is acted upon only by acid and in one way: $Fe+2HX=FeX_2+H_2$. Out in the open, carbonic acid is the effective agent; in towns this may be a variety of acids. If the liquid film in which the action takes place be free from oxygen or reducible substance, the negative element in the couple (carbide or other active impurity in the iron) is soon polarised and the action takes place irregularly and slowly. If, by the intervention of dissolved oxygen, the polarisation be prevented, action will not only be continued but accelerated, owing to the adjuvant effect exercised by this depolariser. Such attack is corrosion but not rusting. Rusting is due to the separation at the surface of the iron, of oxide either from the ferrous salt which is initially produced or from ferric salt formed from this ferrous salt: these salts are continually being

hydrolysed as they are produced. So long as acid can penetrate through to the iron surface, the action must continue. The character of the deposit will depend upon secondary changes, due, usually, to the intervention of oxygen as depolariser.

Water

Of all substances known to us, not only the most active and useful but the most marvellous is water. Without water, apparently, "chemical change," as we know it, could not occur—the world would not merely be lifeless but subject only to "mechanical" decay. The contrasts water affords, in its three states, are shown by no other compound—specially remarkable is the change that attends the passage from the liquid to the solid state, involving a sudden growth in volume of about one-tenth. Some new "planetary system" may well be supposed to come into existence, owing perhaps to a great rearrangement of orbits. When this can be fully explained in terms of electrons, chemists may well begin to take these seriously in their work—not before. The life-history of water is a wonderful story. Commencing with the two gases, hydrogen and oxygen, two of the least coercible that are known to us, on interaction (under the influence of a determinant and probably also of a catalyst), these afford the liquid *water*. Much "energy" is set free in the process, ultimately as heat, the amount developed in the creation of the gramme-molecular proportion (18·016 grammes) being enough to raise the temperature of nearly 700 grammes of water from 0° to 100° C.

What meaning are we to attach to the word *water*, however? It should be reserved for and applied to *the liquid alone*, which undoubtedly is a complex. The fundamental unit molecule, represented by the symbol

OH_2, is best spoken of as *hydrone*. This is a gas under ordinary conditions. The formation of water from this gas may be pictured as a chemical process or interaction in no way distinguishable, in principle, from that involved in the primary interaction of the gases hydrogen and oxygen. Aitken's experiments are held to have proved that the condensation of "aqueous vapour" and the formation of drops of (liquid) water in the atmosphere—of cloud—only take place around a solid nucleus—a catalyst, in fact. It is more than probable, that it will eventually be found and admitted that a *determinant*—a trace of some "salt"—is also necessary. Such impurity is always present, in the form of carbonic acid, nitrous and nitric acids, if not of sulphurous or sulphuric acid, an ammonium salt or sea salt. The nature of the interaction, the composition of the product, is undetermined. Probably, water is a mixture of various liquid components, of *polyhydrones* $(H_2O)_x$, $(H_2O)_y$, etc., saturated with the gas hydrone, OH_2, the proportions of the constituents depending upon the temperature. Even above 4°, the point of maximum density, the liquid must be saturated with ice-molecules; the complexity of these is also undetermined—maybe the hydrone unit simulates the carbon unit and preferentially combines in sixes. It is a matter of interest that "ices" of greater density than ordinary ice may be obtained by subjecting water cooled to very low temperatures to great pressure. All suggestions hitherto advanced as to the composition of "water" molecules, under various conditions, may be regarded as purely speculative.

Water is a specially active solvent of compounds—after its own heart: of compounds of oxygen and of the halogens, in a lesser degree of nitrides (compounds of the ammonia type), not at all of "neutral" compounds of carbon (the hydrocarbons). Dissolution—whatever the

solvent—presumably, is a chemical process, in the main: not a mere intrusion of the dissolved molecules among those of the solvent but the consequence of some degree of "affinity" between the contending molecules. The process cannot, therefore, well be considered without reference to the affinities of molecules and of their constituent atoms.

Affinity and Valency

Hydrogen.—The gas hydrogen, as we know it, is an almost neutral material. It is condensed to a liquid only under high pressure, at a low temperature; the liquid boils at $-253°$. The molecules of hydrogen, therefore, have but little affinity for each other. The molecule is diatomic, being represented by the formula H_2. As the two atoms are firmly held together in the molecule, they must have considerable affinity for each other and nearly satisfy one another: the molecule has but a slight, obvious, *residual* affinity.

Oxygen.—The same may be said of gaseous oxygen. Being far heavier than those of hydrogen, the molecules are, in a measure, less swift in movement and more easily "caught" by other molecules. Oxygen is definitely more active and displays a higher degree of residual affinity. Moreover, we must picture atomic oxygen, like atomic hydrogen, as gifted with intense affinity—with an almost indiscriminating affinity, as excepting the argonides and fluorine, it forms compounds with all the elements, most of which are of a relatively high order of stability. It is a far more companionable element than hydrogen. Bring hydrogen and oxygen together, in presence of the necessary negotiators of change, allow them to interact in the sense of the equation,

$$2H_2 + \varepsilon\delta\kappa + O_2 = 2H_2O + \varepsilon\delta\kappa$$

they give rise to hydrone and eventually to water. These products differ in an astounding way from their generators. The molecule of hydrone has little more than half the mass of that of oxygen, yet—given proper conditions—it condenses, with the greatest ease, to water. Not only so, the amount of energy set free in the interaction of the molecules of hydrone: $x\ OH_2 = (OH_2)_x$, is about one-tenth of that liberated in the original gaseous interaction. The molecules of hydrone are thus shown to be possessed of residual affinity in a far higher degree than is even oxygen. Hydrone, indeed, may be said to be a really active form of oxygen-stuff—far more so than is gaseous oxygen. Hence it is that water is so good a solvent: at least, there are molecules in the liquid mass which are very active, chemically speaking. Water, we shall see, must be regarded as a complex mixture, in which are present molecules of varying degrees of complexity: H_2O, $(H_2O)_x$, $(H_2O)_y$, etc., in proportions which depend upon temperature.

Hydrogen and Chlorine.—Similar considerations apply to hydrogen and chlorine and to hydrogen chloride, the product of their interaction—under appropriate conditions. Although chlorine is much more easily condensed than is oxygen and therefore is to be credited with an even greater store of residual affinity than is oxygen, strange to say, hydrogen chloride, though a more massive molecule than hydrone, has little attraction for itself, being far less easily liquefied than is hydrone; moreover, the liquid is a poor solvent compared with water. Nevertheless, hydrone and hydrogen chloride attract each other irresistibly—the chloride is very soluble in water. We have to consider what the nature of the interaction may be in this and in other cases of dissolution in water.

Nitrogen.—Azote is more extreme in its behaviour than is even hydrogen. The molecule N_2 is all but inert, under

ordinary conditions, yet we have every reason to believe that its component, atomic nitrogen, is gifted with intense affinity. Whereas hydrogen and chlorine, respectively hydrogen and oxygen, interact readily, when merely brought together in presence of the necessary determinant and the mixture is sparked, azote and hydrogen interact only under high pressure, at a fairly elevated temperature and in presence of special catalysts. The interaction, moreover, is very partial: in fact, the product, ammonia, is formed reversibly: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, interaction taking place far more readily backwards than forwards.

Ammonia, like hydrogen chloride, has little affinity for itself, though more easily liquefied than the latter; the liquid has special solvent properties of a most interesting character. The gas is readily dissolved by water but it is easily expelled from the solution. Most characteristic of ammonia is its behaviour with hydrogen chloride: the two interact, when properly impure, on admixture, forming the white crystalline solid, ammonium chloride

$$HCl + \varepsilon\delta + NH_3 = NH_4Cl + \varepsilon\delta$$

a salt which bears the closest possible remembiance to common salt.

Carbon.—Lastly, we have to consider the most attractive to the fair sex of all elementary materials—carbon. We ought to confine this term to the ideal represented by the symbol C—which we cannot directly handle. We only know it in its compound polyatomic form, as diamond: a compound of extraordinary interest. If the chemist were properly mindful of the wondrous power of carbon, as the foundation stone of the organic world, he would wear the biggest diamond procurable—as "mark of the beast." It is customary, in the text-books, to speak

of forms of carbon other than the diamond—to wit, graphite and the charcoal carbons. No proof has yet been given that these are carbon—much may be said in favour of the view that they are but highly condensed hydrocarbons.

Carbon and hydrogen interact only under special conditions—at the high temperature of the electric arc—the product being the gas acetylene, C_2H_2. The simplest "hydrocarbon" is methane, CH_4, known generally as miners' fire damp (*dampf*, vapour) and also as marsh gas, as it is often met with as the product of the natural decay, under the influence of special micro-organisms, of cellulosic materials. Methane is an inert material, in so far that the four affinities of the carbon atom appear to be satisfied by the four hydrogen atoms and, reciprocally, the affinities of the hydrogen atoms by those of the carbon atom: it is one of the least coercible of gases. Derivatives are only to be obtained from it by displacing one or more of the four hydrogen atoms by some equivalent radicle or radicles.

The four hydrides considered, taken in conjunction with hydrogen, form a remarkable series :—

$$H_2 \quad HCl \quad H_2O \quad NH_3 \quad CH_4.$$

Three of these are eminently active compounds, obviously possessed of residual affinity, whilst the fourth, methane, appears to be individually inert: in this compound, carbon and hydrogen, apparently, are mutually *satisfied*. What is to be the conclusion from such evidence? Is it to be, as appears from the behaviour of hydrogen itself and of methane, that the hydrogen atom is a single-minded individual, able to grasp at most a single other atom: that the unsaturated character of the hydrides of chlorine, oxygen and nitrogen is a consequence of the

inability of one, two and three atoms of hydrogen respectively to satisfy the desires of these elements? This, indeed, has long been the opinion of chemists generally. Hydrogen is considered to be a consistently *monadic* or univalent element and those with which it associates are often elements of variable valency, whose desires it cannot fully satisfy. In recent years, the reputation of hydrogen as a simpleton has been impugned —yet not seriously: on careful consideration of the statements made, in the light of the facts, there seems to be little reason as yet to regard them as of more than imaginative value.

The hydrides of fluorine, bromine and iodine—all elements of the chlorine family—are in most respects scarcely to be distinguished from hydrogen chloride.

Water may be said to be entirely peculiar in that the "restraining" effect of hydrogen upon the oxygen atom, in the unit molecule OH_2, is so slight. The hydride of sulphur—the element akin to oxygen and next below it in the oxygen family—although similar to hydrone in composition, hydrogen sulphide, has none of the properties of the oxide. It is gaseous and not easily liquefied and the liquid is a poor solvent. Strangely enough, however, if the hydrogen in the two hydrides be displaced by the hydrocarbon radicle (C_2H_5), compounds are obtained in which the properties are, in a measure, reversed. Ether, $(C_2H_5)_2O$, has little tendency to associate with other compounds. The diethyl sulphide $(C_2H_5)_2S$, however, is readily combined with the iodide C_2H_5I, forming the iodide $S(C_2H_5)_3I$, a beautifully crystalline substance in which sulphur appears to be definitely quadrivalent—like carbon in methane. In short, affinity, the valency of a radicle, like human affection, is clearly a relative rather than an absolute function: valency is a variable, not a constant, at least in many cases. Perhaps the only

element of constant valency is hydrogen—but this i singular in so many ways: this assumption is, at least, : desirable one to make, so long as it cannot be disproved *in fact, it is that upon which our entire system of structura formulae in organic chemistry has been constructed.* Th consistency of that system is so marvellous, that ou confidence in it will not easily be disturbed.

Electrolysis

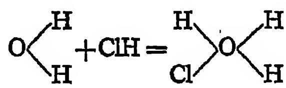
Accepting the conclusion that oxygen has more or less residual affinity when associated with two hydrogen atoms, as it is in hydrone, what interpretation is to be placed upon the process of dissolution in water? What is water, as compared with hydrone? By what act do two diverse liquids give rise, upon admixture, to a solution conducting more or less well, which apart are without the power of acting as electrolytic conductors? When hydrogen chloride is dissolved in water, a highly conducting solution is obtained; when ammonia is similarly dissolved, the conductivity of the solution is low, at best. What is the difference? When hydrogen chloride and ammonia gases are mixed in equal volumes, they at once interact in the sense of the equation

$$NH_3 + \varepsilon\delta + HCl = NH_4Cl + \varepsilon\delta.$$

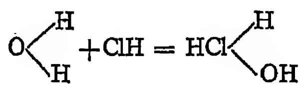
The product is a crystalline solid, a definite compound, the salt ammonium chloride, which most closely resembles common salt, NaCl. We cannot well do otherwise than assume that whilst only tervalent to hydrogen, the nitrogen in ammonia becomes excited to a higher valency, when a fourth *positive* hydrogen atom is offered to it *together* with a fifth *negative* (chlorine) atom. The two molecules, ammonia and hydrogen chloride, do not merely combine but that of the chloride, apparently, *is divided*

and distributed upon the ammonia molecule, the nitrogen functioning as a quinquevalent radicle.

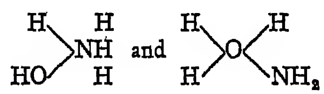
If the same simple assumption be made, the interaction of hydrogen chloride with hydrone, in water, may be represented in the following manner



As, however, oxygen and chlorine are observed to act in a similar and equivalent manner, interaction should also take place as expressed in the equation



The interaction of ammonia and hydrone molecules, in like manner, should give rise to molecules of two kinds,



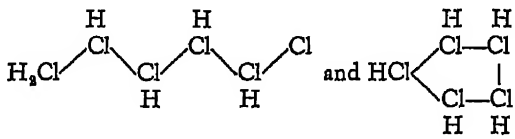
In such compounds, formed by the exercise of secondary affinity, the *negative* radicle in each complex is clearly less firmly held than in the simpler compounds from which it was formed and, therefore, should be more easily separated, we may suppose: the "residual" affinity of this radicle must be greater than it was in the simple molecules. For example, in the complexes formed from hydrogen chloride and hydrone,

$$H_3O{\cdot}Cl \text{ and } H_2Cl{\cdot}OH$$

the chlorine radicle in the one, the hydroxyl in the other, is less firmly held than it was in the original simpler

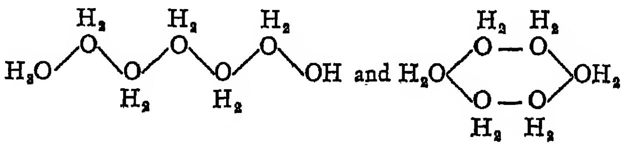
molecule. The atoms are all less firmly knit together in the complexes. Their condition is, perhaps, that sometimes spoken of when such molecules are said to be "electrically charged."

Complexes such as are here contemplated are also formed, it is to be supposed, from the fundamental units which constitute the gaseous substance. On liquefaction these undoubtedly become associated in various ways. Thus, liquefied hydrogen chloride may well be supposed to consist of complexes such as

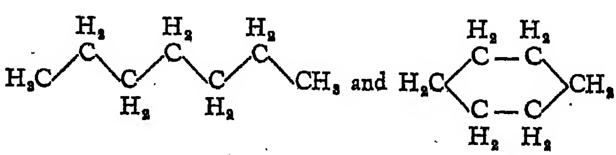


saturated with the simplex HCl. It is impossible to say in what proportions these are present: possibly the one form is dominant.

Water, we may aver, is equally a mixture of the fundamental unit, hydrone, OH_2, with complexes such as



Carbon compounds of these types are well known as stable structures, such as



There is general agreement among chemists and physicists that the carbon compounds are thus constituted.

The angles at which the carbon atoms meet in the diamond, the distance apart of the atomic centres (of the carbon atoms), have been exactly determined, in recent times, by means of X-rays. The carbon atoms meet at $109°28'$, the tetrahedral angle; the centres are little more (1·54) than an Angström unit (one ten-millionth of a millimetre) apart. There is no reason why we should not see, with the mind's eye, in the liquefied hydrides of chlorine, oxygen and nitrogen, a structure such as we have seen, largely with the actual eye, in hydrides of carbon.

Common water will convey or conduct an electric current—electrolytically. The more it be purified, the less readily it conveys the current. *It is logical to assume that water free from every contamination would be a non-conductor.* Such water is an ideal. Water cannot be dealt with apart from a containing vessel: whatever be the nature of the vessel in which it be received and stored, the surface will be more or less contaminated and more or less subject to attack. The " best water " that has been made, has been made in glass and measured in glass—glass we know *is attacked* by water. In testing electrically, platinum electrodes are used—platinum, we know, is an absorptive material and pure platinum is inconceivable as a reality. A *pure* substance is the thing itself—there may be degrees of impurity but not of purity. We are so accustomed to an impure world, that it is difficult to rise into the empyrean of ideal purity: physicists have long been noted for their lack of the sense of cleanliness; chemical sanitation is not yet generally at the height at which it should be—and gullibility, of the order pictured by Carlyle, still plays a large part in our Society. Naughty and undisciplined as we may seem to be, the general tendency is to obey and follow the pretending leader.

To explain the observation that any electromotive force, however small, would produce electrolysis in a solution, causing the ions of the solute, say the hydrogen (H) and chlorine (Cl) of hydrogen chloride (HCl) dissolved in water, to pass to opposite electrodes and there unite and appear as hydrogen (H_2) and chlorine (Cl_2), Clausius long ago "pretended" that some few of the molecules of the chloride "banged themselves to pieces" —so that no work had to be done by the electric current in separating the ions: it only was necessary to give them direction and set the one to wander to the negative, the other to the positive electrode. This electrical test, however, is one of infinite delicacy—no thought has been given *to the fact* that the reduction of the "impurity" at an electrode surface to an extent beyond or even equal to that of the delicacy of the electrical test is a practical impossibility. Chemists have been led to base their faith, the entire theory of chemical change, upon the observations of two German physicists working in the dim and distant past of 40 years ago—both honourable men but both physicists and mathematicians, not practised chemists alive to the need of the most excessive sanitary precautions, if a chemical clean bill of health were to be secured. Helmholtz is supposed to have electrolysed water by means of non-polarised electrodes. In fact, he used two platinum plates and a third plate of palladium charged with hydrogen: his solution was, therefore, necessarily charged with hydrogen and one or other of his plates was "hydrogen polarised."

Arrhenius, in 1884, extended the Clausius hypothesis but dropped his mechanical explanation. To account for the development and increase of electrical conductivity on dissolving a "salt" in water, to an extent varying with the nature and the proportion of salt used, he assumed that the molecules of the dissolved salt just fell to pieces

into separate *electrically charged ions.* Why or wherefore they did so, where the energy to break them up came from, was never explained.

As a matter of fact, what has to be explained is the appearance of electrical conductivity and also of chemical activity on bringing together two substances which, if logic have any meaning, by themselves are inert. Logic seems to indicate some *interaction* as the only possible cause of the change. The electrolytic dissociation school did, after a time, attribute the change to the high "specific inductive capacity" of the solvent—whatever that may mean. Directly the solvent is called in, the explanation becomes chemical, however, not merely mechanical nor based upon a display of mere wilfulness. "We will dissociate, nothing shall prevent us," was the war cry of the molecules, according to Arrhenius. The chemist had more belief in their moral character and that they would observe the marriage tie.

What Arrhenius really did—and the service was a great one at the time—was to lay great stress upon the existence of an active as distinguished from a passive part, in a chemically active medium, by correlating the electrical conductivity developed in a solvent by the addition of a "salt" with the chemical activity of the dissolved substance—assuming the dissolved substance (in the form of its ions) to be the sole agent active. He also developed Kohlrausch's conception of molecular conductivity, as distinct from that of specific activity (of the solution as a whole), by referring the conductivity to the ions of the solute alone and correlating this, to some extent, with chemical activity.

The generalisation came at a time when much attention was being paid to the determination of molecular weights of dissolved substances. Raoult especially had shown that equimolecular proportions of many substances produced

the same effect upon the properties of a solvent: for example in raising the boiling point; moreover, that, within limits, the effect was proportional to the concentration, *at low concentrations*. Van't Hoff also had advanced a kinetic explanation of the phenomena of so-called osmotic pressure—the pressure developed within a cell, containing a solution, by water passing through the lining membrane without the solute passing out.

Osmotic Pressure

The pressure developed within a cell, by the entry of water (as shown by the rise of liquid in a gauge tube attached to the cell) *into dilute solutions*, appears to be the same as would be developed by the entry of a gas, in equivalent amount, into a cell already filled with the gas, at a known pressure, through a wall permeable only by the entering gas. For example, when a cell of palladium (which is permeable by hydrogen and not by nitrogen) filled with nitrogen at atmospheric pressure, is surrounded with hydrogen at atmospheric pressure, the hydrogen passes through until equilibrium is reached—when the hydrogen pressure is the same within and without the vessel: at this stage, the molecules of hydrogen are travelling at equal rates and in equal numbers both ways. The pressure within the vessel is thus raised to two atmospheres—by the addition of the atmosphere of "pressure" due to the hydrogen. Likewise, if a dilute solution, say of x grammes of sugar in 22·3 litres of water, be filled into a finely porous cell provided with a gauge tube and this be plunged into water, the liquid rises in the gauge tube until the pressure is $\frac{x}{342}$ of an atmosphere, 342 being the relative weight of the molecule of sugar. The late Prof. E. F. FitzGerald, a distinguished physicist

of unusual breadth of outlook, speaking of this phenomenon, says :—

"It is a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution if in the gaseous state but to imply that the dynamical theory of the two is at all the same or that the dynamical theory of a gas is in any sense an *explanation* of the law of osmotic pressures is not at all in accordance with what is generally meant by the word 'explanation.' This so-called explanation is not a dynamical explanation at all, it is only a very far-fetched dynamical analogy. These osmotic pressures are much more closely connected with Laplace's internal pressure in a liquid, which is essentially dependent on the forces between the molecules than with the pressure of a gas, which is essentially almost independent of the forces between the molecules. There must be some dynamical reason why the solvent gets through the membrane while the body in solution does not. It must be due to capillary forces between the solid and the molecules of the solvent" (Helmholtz Memorial Lecture, *Chem. Soc. Jour.*, 1896).

An understanding of osmotic phenomena is a matter of great importance, because of the part they play in the exchanges between the cells which constitute living structures: the cell walls acting as discriminating septa.

It should be noted that solutions in water have a lower vapour pressure and therefore a higher boiling point, also a lower freezing point than has water. This is true of solutions generally, whatever the solvent. In fact, all the properties of a solvent are modified by the presence of dissolved matter, whatever its nature may be, the alteration being proportional to the amount dissolved—so long as the solution remain dilute.

The striking contribution made by Arrhenius in discussing van't Hoff's generalisation was in associating the superior, if not abnormal, effect of electrolytes upon the solvent with the increase in molecular electrolytic conductivity of dissolved salts upon dilution. Whereas non-electrolytes produce the unit osmotic effect, molecular proportions producing the same effect, electrolytes have more than unit effect and as the solution is diluted the effect increases, until, in the case of binary compounds such as hydrogen chloride, HCl, for example, the molecular effect is practically doubled—as if the radicles H and Cl were acting independently.

Arrhenius made the assumption that they were, but that the water remained unchanged. It is impossible to grant such an assumption. No valid reason ever has been given which will account for the separation, which is one involving a great absorption of energy. Actually, a not inconsiderable amount of heat is evolved when hydrogen chloride is dissolved in water, part of which, of course, is due to the liquefaction of the gas. Again, the assumption is one that involves a sharp distinction being drawn between hydrogen chloride and hydrone—speaking chemically, this is impossible, what is generally true of the one being true of the other.

The nature of the change which it is conceivable takes place when hydrogen chloride and hydrone interact has already been pictured. In view of the known behaviour of hydrogen chloride towards ammonia, the chemist is in a position to assert that hydrogen chloride and hydrone must be able to interact and do interact in a similar manner. He can produce and exhibit in a crystalline form a compound formed from methylic oxide, $(CH_3)_2O$—the analogue of hydrone—and hydrogen chloride.

The question then arises—how are the alterations in the properties of water and of solvents generally induced

by the presence of a substance in solution to be explained—how, in particular, is the peculiar and enhanced effect of (potential) electrolytes as compared with non-electrolytes to be pictured. The first assumption that may be made is—that, in liquids, the primary, chemically active unit is the simple molecule. In water this is hydrone, OH_2. It will easily be granted that water is saturated with hydrone, the proportion varying with the temperature. As a matter of fact, the vapour pressure of an aqueous solution is lower than that of water. One effect of the solute molecules is, therefore, to capture and restrain a certain proportion of the hydrone molecules. It may be urged that as soon as hydrone molecules are withdrawn, others should come forward—produced by the breaking down of polyhydrones—to take their place and restore the equilibrium. The facts negative this assumption : the dissolved substance exercises an abiding influence. It is almost necessary to assume that the residue of the solvent is modified : that the complexes present along with the simple, fundamental molecule exist in a different proportion : that inasmuch as the freezing point is lowered, the "crystallisable" form is diminished in amount. Water near to its freezing point must be saturated with "ice-molecules" whatever the complexity of these may be. When a substance is dissolved in water, the hydrone solute complexes which are formed—whatever their nature, doubtless exercise a disturbing influence upon the rest of the liquid and the equilibrium is perhaps altered in such a way that fewer "ice-molecules" are present.

As to the peculiar influence of electrolytes—we know that the departure from the "normal" behaviour of non-electrolytes varies with the compound dissolved and the strength of the solution, the specific molecular effect being always greater the more dilute the solution.

Let it be assumed that hydrone and the solute, AB, interact in the following manner

$$\overset{+\,-}{AB} + OH_2 = \overset{+\,-}{AB}\left\langle\begin{array}{l}H\\OH\end{array}\right.$$

$$\overset{+\,-}{AB} + OH_2 = H_2O\left\langle\begin{array}{l}\overset{+}{A}\\\overset{-}{B}\end{array}\right.$$

Each of these products will be an active unit—one that is more active than the molecule from which it is derived—than hydrone on the one hand, than the salt molecule on the other. The relative proportions in which the two are formed will vary with the concentration. In concentrated solutions, however, a large proportion of the salt molecules will not form active complexes but, it may be supposed, will be associated in grouped or closed systems, *e.g.*,

$$AB + 4OH_2 = AB\left\langle\begin{array}{l}\overset{H_2}{O}-\overset{H_2}{O}\\ \phantom{O-{}}| \\ \underset{H_2}{O}-\underset{H_2}{O}\end{array}\right.$$

which are non-valent and only possessed of slight residual affinity.

Non-electrolytes may be regarded as differing from electrolytes in that they are not divisible against hydrone, interactions taking place only in one way

$$\overset{+\,-}{XY} + OH_2 \leftrightharpoons \overset{+\,-}{XY}\left\langle\begin{array}{l}H\\OH\end{array}\right.$$

To explain the enhanced effect of potential electrolytes and the increase of the effect as the solution is more and more diluted is more difficult. As these are effects of dilution, they are clearly due in some way to the action of the water. The solution of the problem suggested by

H. E. Armstrong (*Roy. Soc. Proc.* 1923, vol. A 103, p. 610) is, that when the "couple" formed of the two systems $\mathrm{AB}\Big\langle{}^{\mathrm{H}}_{\mathrm{OH}}$, $\mathrm{H_2O}\Big\langle{}^{\mathrm{A}}_{\mathrm{B}}$ and hydrone (OH_2) is resolved, it may and does give rise to hydronol, $\mathrm{H_2O}\Big\langle{}^{\mathrm{H}}_{\mathrm{OH}}$ —a more active unit even than hydrone itself. Further, that as dilution proceeds, AB is more and more completely resolved against hydrone and converted into $\mathrm{H_2O}\Big\langle{}^{\mathrm{A}}_{\mathrm{B}}$. When this action is complete, AB has exercised its maximum effect. Hydronol, however, being produced concurrently, is ultimately present in an amount equivalent to that in which the system $\mathrm{H_2O}\Big\langle{}^{\mathrm{A}}_{\mathrm{B}}$ is formed. Finally, two active systems are present: if the action be complete, the combined effect they produce is twice the unit effect.

When a solution is placed in contact with water, separated by a diaphragm through which only the water can pass, hydrone is attracted into the solution, molecule for molecule of the active systems present. The so-called osmotic pressure within the cell may be conceived of as due to the directed oscillatory impacts of the hydrone molecules lightly paired with the active systems.

In a sufficiently dilute solution, ultimately, two osmotically active, reciprocal molecules would be produced, at the expense of each single molecule of the salt: in other words, the single molecule of the potential electrolyte, hydrogen chloride, would apparently have double the effect of a single molecule of a non-electrolyte.

Assuming that electrolysis involve the interaction of two diverse "distributed" systems, under the influence of an electromotive force, the (molecular) conductivity of the dissolved chloride would also be at its maximum in the fully diluted liquid.

Solutions

The activities operative within solutions are too little considered. They are best realised by studying the interactions of soluble salts. When, for example, potassium chloride and magnesium sulphate, $MgSO_4 \cdot 7H_2O$, are dissolved in equivalent proportions and the solution is sufficiently concentrated, a large amount of the double sulphate $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$, gradually crystallises out. It follows that much of the chloride is converted into sulphate and of the sulphate into chloride; in fact, magnesium chloride is ultimately obtained from the liquid. Often, in such cases, a number of double salts and of salts with varying amounts of water of crystallisation are produced, the product varying with the concentration and relative proportions of the materials present. The presence of the variety of salts met with in natural salt deposits, such as those in Alsace and Hanover, is thus accounted for.

Finally, it may be urged that extreme caution is required in dealing with the problems of solution, because of the fact that the molecules are crowded together. Whatever seeming analogies their behaviour may present with that of the gaseous state, the effects cannot be really gaseous effects—as intermolecular affinities come into play which are practically excluded in the gas.

The conclusions deduced by studying solutions made by dissolving substances all to the same volume—a method in no way comparable with that involved in dealing with

equal volumes of gases—are obviously not comparable, as the molecular proportions in which solute and solvent are present will vary more or less, according to the nature of the dissolved substance. Most of the peculiarities to which attention has been directed are traceable to this illogical practice. Only the very dilute solutions prepared in this manner will afford comparable results. On the other hand, if the molecular proportions of solvent and solute be kept constant, there is always the difficulty that the ultimate volumes vary—that the volume occupied within the solvent by the solute is subject to variation. In fine, it would seem to be impossible to make any strict comparison of solutions—the conclusions must always be open to many corrections.

Electrolysis of "Water"

The production of hydrone by the interaction of hydrogen and oxygen has already been discussed. The inverse change must be subject to similar conditions. Water itself and by itself cannot be electrolysed—*ex hypothesi*, it has no conducting power. To speak of the production of hydrogen and oxygen by electrolysis, as if the process were simple and direct, is as wrong as to speak of the production of water itself from oxygen and hydrogen : the electrode face must be the seat of a whole series of changes. Without considering the nature of the internal process (within the liquid), it may be assumed that the complex $\mathrm{HX}{<}^{\mathrm{H}}_{\mathrm{OH}}$ (formed from the acid HX) at the one electrode surface is initially converted into a perhydrol

$$\mathrm{HX}{<}^{\mathrm{H}}_{\mathrm{OH}} + 2\,(\mathrm{OH}) = \mathrm{HX}{<}^{\mathrm{H}}_{\mathrm{O{\cdot}OH}} + \mathrm{OH_2}.$$

Such compounds are well recognised products of electrolysis. At times, they undergo hydrolysis and perhydrone HO·OH is formed but, apparently, is never an initial product.

At high concentrations and particularly at high current densities, the attack by OH becomes more and more concentrated upon the molecule and probably higher perhydrols are formed, which break up at the electrode surface into either oxygen or ozone—whether directly or owing to hydrolysis or perhydrolysis.

Acidity: Apparent and Effective

The term *acid* has long been a bone of contention among chemists and there is great need of a clear understanding on the subject. A Latin term, the equivalent of the Teutonic *sour*, it appeals to the ear and is familiar because of the occurrence of acids in foodstuffs—in vinegar, fruit, etc. The opposite of an acid—an alkali or base—in the sense that it will neutralise the acid and destroy its sourness to the palate—is unfamiliar, as such substances are not in ordinary use, at least in connection with food. When acid and " base " interact, a salt is formed : the base, however, is no more *the base* of the salt than is the acid : it happens to have been so-called, only because " acid " was already appropriated and had a distinct, identifiable meaning. " Alkali " has no etymological significance in itself and the conventional use of base is misleading when thus transferred to chemical practice.

Acids were known long before the isolation of the vital principle of air. When this was isolated, Lavoisier gave it the name oxygen, because the oxides formed on burning common combustibles, such as carbon, sulphur and phosphorus, were " acid."

The oxides of the non-metallic elements then became known as acids. To the present day, the public speaks of the acidic oxide of carbon as carbonic acid, a far better name for general use than that of the chemist, carbon dioxide, which by a silly and most reprehensible practice is now often converted into *See-Oh-Too* (CO_2), especially in biological circles. Formulae should never be used as spoken words. Lavoisier supposed that acids generally contained oxygen and, on this account, being a constituent of muriatic acid, chlorine was supposed to be an oxygen compound. When this was disproved by Davy and "spirit of salt" was shown to consist simply of hydrogen and chlorine, the swing of the pendulum set in and acids were defined to be compounds of hydrogen (hydrogen salts) in which the hydrogen could be displaced by metal, if not directly, through the agency of a metallic oxide or base. The name sulphuric acid was then transferred from the oxide SO_3 to the hydrate, $SO_3 + OH_2 = H_2SO_4$, oil of vitriol or vitriolic acid, as it was long called. Fifty years or so ago, there were two contending schools —one calling the oxide the acid and the hydrate either simply monohydrate (a name long used in commerce) or hydric sulphate. A salt was said to be formed by the union of acid and base and, in hydric sulphate, hydrone was supposed to take the place of the base soda in sodic sulphate: the acid, in fact, was regarded as a hydrogen salt.

The other school regarded a salt as derived from its acid by the displacement of hydrogen and the hydrogen as itself present in the form of hydroxyl (OH). The halhydrides were again treated as peculiar. The basicity, we may say equally well the acidity, of an acid varies with the number of displaceable hydrogen atoms. Phosphoric acid H_3PO_4 has long been supposed to be an acid in which the three atoms of hydrogen are of different value but sulphuric acid has almost always been formulated

as if the two hydrogen atoms were alike in function. It has been customary to represent the latter acid as symmetrically constituted—$(SO_2)\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}$. When the matter is studied historically, it is clear that this view is largely an academic conclusion. No significant evidence of structure can be adduced in proof of such a formula and we must admit that we do not exactly know how the acid is constituted—simple as it is.

The issue is complicated by the fact that "acids" vary greatly in strength—some are "strong," the majority are weak. Defining *apparent acidity* as the equivalent proportion of "acid" present in a solution, which is measured by determining the amount of standardised alkali required to neutralise the liquid, the *effective acidity* is measured by using the acid as a hydrolytic agent, for example, in effecting the resolution of cane sugar into glucose and fructose:—

$$C_{12}H_{22}O_{11} + OH_2 = 2C_6H_{12}O_6.$$

The activity of an acid such as acetic, contrasted with that of an equivalent amount of chlorhydric or nitric, is very slight—it has not one two-hundredth of the strength of these strong acids as a hydrolytic agent. There is very little, if any, doubt that the explanation of this fact is, that but little of the acetic "acid" becomes real and active. On the other hand, almost the whole of the dissolved hydrogen chloride in muriatic acid seems to be in the active state—as the electrolytic conductivity, referred to the molecular proportion of hydrogen chloride present, is relatively little changed and increased by high dilution. Nearly 90% of the chloride appears to be present as the active acid even at low dilutions.

Instead of representing real or effective acidity as a

fraction of the apparent acidity, thus avoiding the introduction of any hypothetical interpretation of the facts, an unfortunate practice has grown up of representing real acidity in terms of "hydrogen-ion-concentrations." Nay, worse, the hydrolytic effect has been represented as due to the hydrogen ion and not to the two ions of the acid acting in conjunction. Terms are thus used which only the elect can understand—which is undesirable in all interests. At the moment, the term acid has no clearly defined meaning.

Much light is thrown upon the nature of multiacidic (multi-basic) acids by the study of their action as hydrolytic agents. Especially is this true of sulphuric acid. This acid readily acts upon a variety of hydrocarbons and other compounds, forming *sulphonic acids*, e.g.,

$$C_6H_6 + H_2SO_4 = C_6H_5{\cdot}SO_3H + OH_2.$$

The sulphonic acids are strong unibasic acids. It is usually said that they are formed simply by the displacement of one of the two hydroxyl groups (OH) in sulphuric acid by a hydrocarbon or similar radicle. If so and the two (OH) groups be of equal value, the sulphonic acids, it might reasonably be supposed, should have about half the effective strength of sulphuric acid. As a matter of fact, tested by cane sugar, they have little less than 90% of its strength. Hence, it would seem probable, that sulphuric acid is in reality uniacid (unibasic) but has a slight residual acidity. The argument may be extended to all multi-acid inorganic acids. These seem to be comparable with lactic acid, $CH_3{\cdot}CH(OH){\cdot}COOH$, which from early times has ranked as part alcohol, part acid—as essentially uniacidic. The argument is of consequence as pointing to some dissymmetry in the structure of sulphuric, carbonic and other multiacidic acids. (Compare *Roy. Soc. Proc.* 1914, A vol. 90, p. 73.)

The Correlation of Function and Structure

Having thus considered a case in which function and structure are clearly in close connection, attention may now be directed to carbon compounds, which afford a vast mass of evidence of the absolute correlation of function with structure.

The structural basis of chemistry is very simple—one of astounding simplicity, in fact. It is expressed in the fixed series:

$$HCl, H_2O, H_3N, H_4C.$$

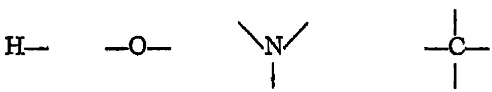
Taking the hydrogen atom as unit, the atom-fixing power or valency of the four elements indicated is one-, two-, three-, four-fold. Chlorine and its analogues are monads, oxygen and its analogues dyads, nitrogen and its analogues triads, carbon and its analogues tetrads. All other elements (excepting the inert) fall into one or other of the four classes. The facts generally of chemistry show that hydrogen is consistently a monad. The facts generally also show that carbon *never exceeds* the tetradic power of which CH_4 is witness. The other elements and their analogues are not so fixed in their affections. Thus nitrogen, in the ammonium compounds, such as ammonium chloride NH_4Cl, carries two additional units, five in all. Oxygen and chlorine also may carry two additional units but their hold upon these is never so firm as is that of nitrogen. The problem of varying valency (atom-fixing power) has given rise to much discussion, over a long period of years: it is in no way ended. At one time, the view was held that in ammonium chloride, the two molecules H_3N and HCl, were still existent, as radicles; such compounds were in consequence termed "molecular." Phosphorus pentachloride, PCl_5, in like manner, was thought to be a compound of the chloride

PCl_3 with a molecule of chlorine Cl_2. Of late years, the alternative view has prevailed, that the two molecules interact and do not merely "associate," so that the units are distributed and arranged about a central atom.

Chemistry, however, is an art as much as a science and the chemist is full of feeling which cannot be quantified. He is satisfied that, in some way, there is a difference which he is in no way yet able to define between the two orders of compounds. Fancy pictures have been drawn of late, in terms of the electronic hypothesis, to represent the two kinds—but these are but paraphrase and as they carry us no further are premature. At most, we know, from the behaviour on electrolysis, that the various atoms carry atomic electric charges (electrons) corresponding to the primary valency—the hydrogen atom one, oxygen two, nitrogen three. The evidence thus far seems to be against the view that the atomic charges may be varied: what then is to be our explanation of secondary valency and still further of the residual affinity which is manifest when secondary affinities are engaged?

No compounds, not even the inert gases, helium, etc., nor hydrogen, methane, etc., are entirely without attractive power or affinity. If they were, they would not be liquefiable. All display a certain amount of *residual affinity*: in other words, whatever the nature of primary and also of secondary affinities, some affinity is left over in the compounds in which such affinities are exercised.

In the early days of structural formulae, chemists were satisfied with plane representations upon paper, in which lines were drawn proceeding from the symbol of the element in accordance with its valency, thus



Then models were constructed of balls with holes drilled into them, in number according to the valency of the elements represented. Other atoms were attached by inserting rods into the holes in the balls. No attempt was made to give any special direction in space to the affinities thus signified. Gradually, it was realised that such formulae and models implied both too much and too little. On the one hand, they gave rise to expectations which were not fulfilled. Thus, two pictures can be drawn of a compound of the type CH_2Cl_2

In the one, the two atoms of chlorine are *opposite*, in the other they are *contiguous*. Exhaustive inquiry failed to discover any difference in the compound, however prepared. On the other hand, many compounds were found to exist which were of the same composition but structurally similar—differing only in one peculiar respect: in that one was the morphological and optical opposite of the other. When the crystal of the one form was compared with that of the other, they were seen to be identical, except that the one was a mirror-image of the other, as a right hand to a left hand. There was a corresponding difference in the behaviour of solutions of the two compounds in plane polarised light—the rays of light being twisted in one direction by the one, equally (if the solutions were of identical strength) in the opposite direction by the other. This was Pasteur's great discovery, made in 1848. Van't Hoff, in 1875, building upon Pasteur's suggestion, that such compounds were geometrically different in structure, resuscitated and expanded Pasteur's suggestion that carbon was itself a

tetrahedral unit and in his *Chemistry in Space* fully developed a doctrine of spatial structure already foreshadowed by Kekulé, which has proved to be very generally applicable. Representing carbon by a regular tetrahedron (such as may be made by joining together four equilateral triangles), he drew attention to the well-known fact, that if one, two or three faces only were different, two being alike, object and mirror image were alike—they could be superposed. If all four faces were different, the image could not be superposed upon the object—such compounds were asymmetric, their models could not be halved, as could those in which only two or three faces were different. He was able to show that all known optically active compounds might be regarded as constituted in the manner suggested and to predict that all such compounds would be optically active. His forecast has been verified in all respects.

Van't Hoff represented the four affinities of carbon as proceeding from the centre of mass of the regular tetrahedron to the four solid angles. They therefore meet at an angle of 109°28′. He represented compounds in which carbon atoms were united by single affinities by tetrahedra joined at their apices—not as filling space. Sir William Bragg has shown, by means of X-rays, that in the diamond the atoms of carbon are thus related—each being surrounded by four others, each of the four meeting it at the tetrahedral angle. A model of the diamond—a sheet of atoms in the diamond—may be made by arranging cardboard tetrahedra side by side, placed alternately base downward and base upward (choosing any face arbitrarily as base). The van't Hoff generalisation has thus been verified in its entirety in principle.

Van't Hoff doubtless found more than sufficient material needing discussion to extend his explanation and correlate it with the crystalline form of solids. The

"solid significance" of the doctrine was never considered by him. Before dealing with this, it is desirable, however, to consider certain peculiarities in the behaviour of carbon.

The Hydrocarbons

The atoms of most of the elements seem to be capable of uniting with themselves and even with others only in very limited numbers. The number of carbon atoms which can unite with one another, however, appears to be illimitable and there seems to be no falling off in grip as the number grows. The simplest hydride, CH_4, is but the beginning of a long series of hydrocarbons, known as the *Paraffins*, in all of which carbon and hydrogen are present in the relative proportions in which they occur in methane, so that they may be represented by the general formula C_nH_{2n+2}. Like methane, these are all *saturated*, in the sense that they do not combine with any substance whatever. The name paraffin is derived from the fact, that especially chemically they have little affinity for chemical agents in general. They may be oxidised, they are acted upon by chlorine and bromine, yet not easily. They yield only *substitution* derivatives, *i.e.*, one or more hydrogen atoms are exchanged for an equivalent radicle. Thus—

$$
\begin{aligned}
CH_4 &+ Cl_2 = CH_3Cl + HCl\\
CH_3Cl &+ Cl_2 = CH_2Cl_2 + HCl\\
CH_2Cl_2 &+ Cl_2 = CHCl_3 + HCl\\
CHCl_3 &+ Cl_2 = CCl_4 + HCl
\end{aligned}
$$

The solid paraffin, used in making candles, is a mixture of higher members of the series. Petrol contains low terms—such as hexane, C_6H_{14}, heptane, C_7H_{16}, etc.—the illuminating and lubricating oils from petroleum are mixtures of terms intermediate between those in petrol and paraffin.

Organic chemistry has often been spoken of as the chemistry of the hydrocarbons and their derivatives, because all other compounds may be derived from the hydrocarbons by processes of simple substitution, by the introduction of various simple atoms or compound radicles (groups of atoms) in place of one or more of the hydrogen atoms of the hydrocarbon.

The paraffin hydrocarbons may be built up to any desired degree of complexity by various simple methods. Thus methane is converted into methylmethane or ethane by the process indicated in the equation :

$$CH_3I + CH_3I + 2Na = CH_3{\cdot}CH_3 + 2NaI$$

Ethane is converted into the next term, propane, in a similar manner :

$$CH_3I + CH_3{\cdot}CH_2I + 2Na = CH_3{\cdot}CH_2{\cdot}CH_3 + 2NaI$$

or into tetrane :

$$CH_3{\cdot}CH_2I + CH_3{\cdot}CH_2I + 2Na = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + 2NaI$$

It will easily be seen that there are two ways of introducing CH_3 (methyl) into propane :

$$\underset{\text{Tetrane}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \longleftarrow \underset{\text{Propane}}{CH_3{\cdot}CH_2{\cdot}CH_3} \longrightarrow \underset{\text{Isotetrane}}{CH_3{\cdot}CH(CH_3)_2}$$

In one the " chain " is simply extended, in the other, two links are associated with the one terminal link. Three and even four links may be attached to one carbon atom, as in trimethylmethane $CH(CH_3)_3$ and tetramethylmethane $C(CH_3)_4$.

Compounds of the same gross or molecular formula, differing in structure, are termed *isomeric*. The successive terms in the series are termed homologues. They are homologous in the sense, that apart from differences in

physical properties, boiling point, density, etc., they are generally alike in their chemical behaviour. This is true also of the isomeric hydrocarbons.

Hydrocarbons are all more or less easily attacked by chlorine or bromine but not by iodine; the iodo-derivatives are obtained by indirect methods.

They are also easily oxidised but the product is often, if not usually, a mixture, as the products are more easily oxidisable than the original hydrocarbons. We speak of oxidation but in reality the process is always initially *one of hydroxylation* and, for the sake of simplicity, may be represented as effected by perhydrone, H_2O_2. Thus ethane is converted into ordinary fermentation or ethylic alcohol:

$$CH_3{\cdot}CH_3 + HO{\cdot}OH = CH_3{\cdot}CH_2(OH) + HOH$$

The primary product of the oxidation of methane, in like manner, is methylic alcohol—the alcohol of wood spirit

$$CH_4 + HO{\cdot}OH = CH_3{\cdot}OH + HOH$$

The alcohols are the organic analogues of caustic soda (sodic hydroxide) thus—

$$Na{\cdot}OH + HCl = NaCl + HOH$$
$$C_2H_5{\cdot}OH + HCl = C_2H_5Cl + HOH$$

This is true if only the hydroxylic (OH) radicle be considered. In the carbon compound, however, the hydrocarbon radicle is also attackable, as in the oxidation process:

$$CH_3{\cdot}CH_2{\cdot}OH + HO{\cdot}OH = CH_3{\cdot}CH(OH)_2 + OH_2$$
$$CH_3{\cdot}CH_2{\cdot}OH + HO{\cdot}OH = CH_2(OH){\cdot}CH_2(OH) + OH_2$$

Both actions take place, according as one or other oxidising agent be used. The two products differ in a characteristic manner, the one being unstable, the other

stable. Whenever two hydroxyls are associated with a single carbon atom, the product is unstable, readily losing the elements of a molecule of hydrone

$$\underset{\text{aldehydrol}}{CH_3{\cdot}CH(OH)_2} = \underset{\text{aldehyde}}{CH_3{\cdot}COH} + OH_2$$

In aldehyde, the dyad oxygen atom takes the place of two monad hydrogen atoms in the hydrocarbon and of the two monad hydroxyl radicles in the alcohol which is the initial product of hydroxylation. Hydroxylation may be carried a stage further

$$CH_3{\cdot}CH(OH)_2 + HO{\cdot}OH = CH_3{\cdot}C(OH)_3 + OH_2$$

The trihydrol thus formed is even less stable than the dihydrol and easily loses hydrone

$$CH_3{\cdot}C(OH)_3 = CH_3{\cdot}CO(OH) + OH_2$$

The product, acetic acid, is methane in which a single atom of hydrogen is displaced by the radicle *carboxyl*, CO(OH). This radicle is characteristic of organic acids generally—the term acid is given only to compounds which contain it or an equivalent radicle, such as SO_3H.

Methane may be oxidised in the following manner :—

$$\begin{aligned}
CH_4 + HO{\cdot}OH &= \underset{\substack{\text{Methylic}\\ \text{alcohol}}}{CH_3{\cdot}OH} + OH_2\\
CH_3(OH) + HO{\cdot}OH &= \underset{\substack{\text{Formalde-}\\ \text{hydrol}}}{CH_2(OH)_2} + OH_2\\
CH_2(OH)_2 + HO{\cdot}OH &= \underset{\substack{\text{Formacid-}\\ \text{hydrol}}}{CH(OH)_3} + OH_2\\
CH(OH)_3 + HO{\cdot}OH &= \underset{\substack{\text{Ortho-}\\ \text{carbonic acid}}}{C(OH)_4} + OH_2
\end{aligned}$$

Formaldehydrol passes by dehydration into formaldehyde, CH_2O, formacidhydrol into formic acid, ortho-carbonic acid into carbonic acid, $CO(OH)_2$, ultimately into carbon dioxide.

The possibility of the formation of isomeric compounds must not be overlooked. Thus, propane may be hydroxylised only to two monohydric alcohols but each of these may conceivably be oxidised in several ways, thus

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CH(OH){\cdot}CH_3$
Propylic alcohol	Isopropylic alcohol
$CH_2(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$
$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}C(OH)_2{\cdot}CH_3$
$CH_3{\cdot}CH_2{\cdot}CH(OH)_2$	

These dihydric alcohols are all known, though they are not produced exactly in the manner indicated. Attention should be drawn to the isomeric compounds

$$CH_3{\cdot}CH_2{\cdot}CH(OH)_2 \qquad\qquad CH_3{\cdot}C(OH)_2{\cdot}CH_3$$

Deprived of hydrone, these yield

$CH_3{\cdot}CH_2{\cdot}COH$	$CH_3{\cdot}CO{\cdot}CH_3$
propionic aldehyde	acetone

both keto-compounds, closely related in character, the one, however, an aldehyde, the other a ketone. The difference between these is particularly well brought out by their behaviour on oxidation

$$CH_3{\cdot}CH_2{\cdot}CH(OH)_2 + HO{\cdot}OH = CH_3{\cdot}CH_2{\cdot}C(OH)_3 + OH_2$$
$$CH_3{\cdot}C(OH)_2{\cdot}CH_3 + HO{\cdot}OH = CH_3{\cdot}C(OH)_3 + CH_3{\cdot}OH$$

The one yields the corresponding acid, a characteristic of aldehydes, the other is broken down. Actually, the methylic alcohol shown in the equation is further

oxidised as it is produced and escapes recognition. Both propaneglycols should yield a stable trihydric alcohol on further hydroxylation

$$CH_2(OH)\cdot CH_2\cdot CH_2(OH) \quad CH_2(OH)\cdot CH(OH)\cdot CH_3$$
$$\searrow CH_2(OH)\cdot CH(OH)\cdot CH_2(OH) \swarrow$$

Actually, this change has not been realised but the alcohol indicated is the well-known substance glycerol (glycerine), obtained as a by-product in making soap, by saponifying hard animal fats and fatty oils with caustic soda.

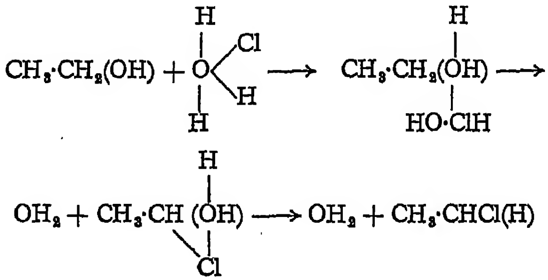
Reduction

Hydroxylation (oxidation) is the process involving the displacement of hydrogen by hydroxyl (OH) ; it is one of the most important of natural processes, especially of those in a downgrade direction. The reverse operation, the displacement of hydroxyl by hydrogen—reduction—is equally frequent and important, especially in upgrade changes. More often than not the two occur, if not in conjunction, in rapid succession. All the changes above considered are reversible by hydrogen (atomic) acting "in circuit" with the hydroxy compound.

Hydroxylic Interactions

Although similar in their functions to metallic hydroxides, the alcohols are in one respect strikingly singular in their behaviour, inasmuch as they do not give rise to conducting solutions when dissolved in water. Metallic hydroxides and acids interact immediately; alcohols are but slowly attacked by acids. The *apparent* outcome of the interaction of alcohol and acid is the substitution of the acid radicle for the hydroxylic radicle. Actually, the interaction may be more complex and

involve a structural change. To give a specific illustration, alcohol and hydrogen chloride do not interact except in the presence of water. Hydrogen chloride and water together, however, form an electrolyte. The process of interaction, in their presence in association (as a composite electrolyte), may be less direct and more complex than is commonly supposed, perhaps broadly as follows :—



The H in brackets is that which may be supposed to take the place of (OH) originally in the alcohol. Some such process as this may be at the root of the Walden inversion, in which an asymmetric compound is produced of opposite sign to that taken, the change being reversed when the inverse interaction is effected. It is probable that such " inversions " often happen unperceived and that not a few inferences of structure may be affected by their occurrence, particularly in the sugar group. The active part taken by " a neighbouring hydrogen atom " may also be at the root of the " steric " hindrance observed in " etherifications."

Unsaturated Hydrocarbons

As soon as hydroxyl is introduced into a saturated hydrocarbon—one in which the four affinities of the carbon atom are separately satisfied—a condition of

instability is established. The hydroxyl tends to separate with hydrogen as hydrone—thus alcohol gives ethylene,

$$C_2H_5 \cdot OH = C_2H_4 + OH_2.$$

" Dehydration," in reality, is an indirect process and may be effected in various ways, as by heating alcohol with either sulphuric or phosphoric acid : a sulphate or phosphate is first formed and decomposed. The loss of OH and H by alcohol is equivalent to the withdrawal of two atoms of hydrogen from the hydrocarbon ethane, C_2H_6. The operation may be repeated—ethylene may be converted into acetylene, C_2H_2, now a common frequenter of society in company of the motorist and largely used in welding and cutting steel. It is also made more directly by heating carbon together with lime, CaO, in an electric furnace, so producing calcium carbide, CaC_2, which is transformed back into lime and acetylene by the action of hydrone (water) thus :

$$CaC_2 + OH_2 = CaO + C_2H_2$$

Ethylene differs by two units, acetylene by four, of affinity from ethane. Both hydrocarbons combine with bromine, giving rise to compounds of the ethane type, $C_2H_4Br_2$ and $C_2H_2Br_4$. The structure of these unsaturated hydrocarbons is not yet settled. Frankland said originally : " Let it be assumed that two affinities of the one satisfy two affinities of the other carbon atom in ethylene, three of the one three of the other in acetylene —write $H_2C{=}CH_2$ and $HC{\equiv}CH$." It *was* so assumed— the conception was simple and easily committed to memory. Van't Hoff said, join two tetrahedra edge to edge to represent the carbon in ethylene, solid-face to solid-face to represent acetylene : the mandate was obeyed, so open to suggestion are we.

Whether or no such conjunction be possible, the fact

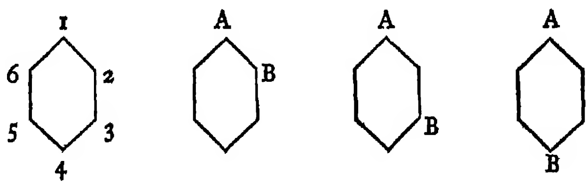
remains that both compounds behave as if they were *un*saturated and full of energy. Julius Thomsen, as the result of his determinations of "heats of formation," has contended that actually no more work is done in "doubly"-combining two carbon atoms, even less in "trebly"-combining them, than in combining them by single affinities. For the present, it is better to term the one "*linkage*" ethenoid, the other *acet(yl)enoid*, than double or treble bonded. The ethenoid linkage is commonly repeated but not the acetenoid.

The paraffins (C_nH_{2n+2}) and the corresponding *ethenes* (C_nH_{2n}) and *acetenes* (C_nH_{2n-2}) are all open-chain hydrocarbons. In the paraffins, carbon atom is united to carbon atom in a continuous series, we may now say, in a zigzag, each setting to the other at the tetrahedral angle $109° 28'$. This conception is found to be in agreement with the verdict given by X-rays.

Phenoid Carbon

A change comes over the scene as more and more hydrogen is removed and the compounds become less and less saturated algebraically. Faraday, a hundred years ago, discovered in the liquid condensed from "oil gas"—the gas obtained by decomposing oil at a red heat—the hydrocarbon C_6H_6, which is now known as benzene. Theoretically, it is derived from the paraffin hexane, C_6H_{14}, one of the chief constituents of petrol of low boiling point. It is a highly refractive liquid, whence the name *Phene*, which was given to it by Laurent, obvious to-day in phenol (carbolic acid). It crystallises readily. Benzene is nearly *saturated*. Chemists account for this fact by supposing the six carbon atoms to be arranged in a "closed chain or ring" and that each carries a single hydrogen atom.

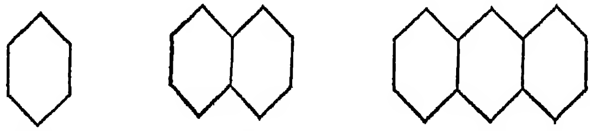
The distribution of the fourth affinities has given rise to much controversy, in large part futile, because no clear conceptions were behind it and discussion was based upon imperfect appreciation of the facts. Chemical formulae, in the main, are but symbols of character—" shorthand " expressions indicative of the general behaviour of the compounds represented. They also portray the general structural relationships or arrangement of the atoms. They do so, however, only in terms of certain conventions. It has been customary to represent ethylene as $H_2C{=}CH_2$. To represent benzene as containing three pairs of carbon atoms related as in ethylene, which is often done, is to use a symbol that is in no way an expression of the facts. The general chemical behaviour of the hydrocarbon is that of a but weakly, not of a highly, unsaturated compound and it is obviously peculiar in its behaviour. Fortunately, the extraordinarily complex chapter of the chemistry of benzene derivatives may be written irrespective of the structure of the hydrocarbon. Regarding it as a closed system, with six symmetrically arranged hydrogen atoms, all that is necessary is to represent it by a regular hexagon with H written at each of the corners. Derivatives are formed by displacing one or more of these hydrogen atoms : when several are displaced the derivatives vary in character according to the relative positions of the displacing radicles—these are easily indicated by numbering the positions relatively to some one, thus :



The relationship of thousands upon thousands of com-

pounds may be satisfactorily represented by this simple device.

By, as it were, soldering phene upon phene, polyphenes of any desired complexity may be produced. Coal tar contains three such.



benzene C_6H_6 naphthalene $C_{10}H_8$ anthracene $C_{14}H_{10}$

These are the foundation stones upon which the great modern dyestuff industry is built. The various "chars" (charcoals) are probably highly complex compounds with but a very small number (in proportion to the carbon atoms) of hydrogen atoms, which prevent the carbons from lapsing into the diamond state.

Diamond is one great carbon-phene—the benzene unit is but a small, highly symmetrical block dissected out from a single layer of atoms in the diamond and clothed with six hydrogen atoms.

Geometric Models

To obtain a model of the diamond, it is only necessary to make a considerable number of regular tetrahedral groups of equal spheres and to arrange these interlocked in sheets, placing them alternately upon base and upon apex, then piling sheet upon sheet, all closely interlocked. Each unit tetrahedral group within such a close-packed mass will be equally surrounded with four other like tetrahedral groups interlocked in *face contact*. Each face-centre between two blocks being a centre of affinity, the model will embody the conception that the carbon atom

has four equal affinities ranging outwards and operating, in so far as other carbon atoms are concerned, at the tetrahedral angle, from the centre of the mass to the face-centres. Occasion may be here taken to point out that the individual atoms at the surface of any mass of diamond must each have an affinity free. This must be true of many compounds. It does not follow, however, that such affinities have their full force.

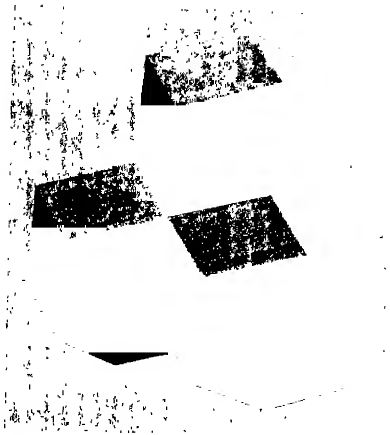
An attempt to correlate crystalline form with chemical structure and develop solid models of complex carbon compounds was first made by Barlow and Pope in 1899.

They advanced two primary propositions—first, that valency may be given volume significance. Taking an arbitrary sphere of unit volume to represent a monad atom such as that of hydrogen, a sphere of twice the volume was used to represent a dyad atom such as oxygen, one of thrice the volume to represent a triad (nitrogen) and one of quadruple volume to represent the tetrad carbon. Second, that the relative valency volume remained the same in a series of related (corresponding) compounds, though the absolute volume might vary. This assumption is made to satisfy the facts of isomorphism—for example, in a series such as that of the three halides, NaCl, NaBr, NaI. If the densities of these salts, referred to molecular proportions—the volume occupied by the gramme molecular proportion—be taken and the assumption made that the sodium maintains its relative volume in the three compounds, the volume increases from chlorine to iodine. This is true generally. Pope and Barlow assumed, however, that there was mutual adjustment and that the 1:1 volume ratio was retained in all the compounds. This is not only rational but apparently necessary.

Unfortunately, the use of spheres varying in volume entailed the construction of models on which the units

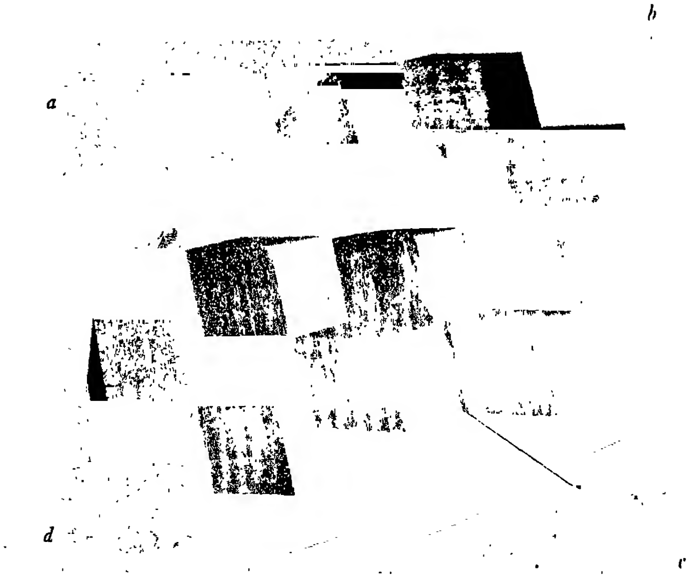
were not close packed and the attempt was unsuccessful on this account.

Mr. Barlow has elaborated a simpler method of treatment which appears to satisfy the conditions to be met. Using a sphere as unit of valency, the dyad is represented by two, the triad by three, the tetrad by four such spheres. Models so constructed can be "close packed" to any extent. If a mass of spheres be compressed, the units are ultimately reduced to dodecahedra and are then in contact over their entire surface. Mr. Barlow adopts such a dodecahedral unit in constructing his models. The carbon atom is represented by a pyramid of four dodecahedra. When two such are brought together to represent atoms united as in the diamond, the faces interlocked may be said to be *terfaces*, as surfaces of three of the four constituent units of the tetrahedron are present. A series of tetrahedra united in this manner, in a rectilinear zigzag, represents the paraffin structure. Lines drawn between the mass-centres of contiguous units meet at the tetrahedral angle in a zigzag. Whilst such straight chains may be dissected out of a sheet of diamond atoms to form the paraffins and their derivatives generally, benzene and the phenoid compounds may be built up from hexagonal blocks—sets of six carbon units—dissected out from the diamond sheet. To produce the benzene model, three "sameway" oriented tetrahedra are placed symmetrically, each resting upon a surface, apex meeting apex at a common centre; then, three other similarly arranged tetrahedra are placed upon these, so that each rests upon an apex, thus filling the three spaces between the lower three, the six together forming a block in which three affinities appear at the upper and three at the lower surface, each of the carbon units in the mass being united to two contiguous units. In such models there are two layers of valency units. To typify benzene, six hydrogen



THE BARLOW TETRAHEDRAL MODEL OF THE CARBON ATOM

Showing left (unshaded) a paraffinic terface, right (fully shaded) a second such face, between these and common to both (partly in shade) an ethenoid surface.



THE CLOSE-PACKED CARBON COMPLEX
IN BENZENE

Showing three inverted tetrahedra, the terfaces of which represent three free paraffinic affinities ranging outwards from the superior surface. In the model of Benzene, three single dodecahedra, representing hydrogen units, are ranged in the upper plane at *a*, *b*, *c*, completing a triangle with five units in each side, resting upon a similar triangle, one of the hydrogen units in which is placed at *d*.

units have to be attached around the hexagon, one being assigned to each carbon atom and alternately placed one in the lower, the other in the upper plane of valency units. The engaged affinities are thus all operative in two planes, as it were.

Mr. Barlow has thus constructed solid, close-packed geometric models of a large number of benzene derivatives, taking into account the crystallographic data. In all but a few cases the models are a direct representation of the compound. In some instances, notably in that of parabromophenol, to obtain a model which is in harmony with the crystallographic data, it is necessary to effect a slight readjustment of some of the units attached to the carbon complex, which remains fixed and unvariable. The shift is of an entirely rational and simple character. The hydrogen unit remains attached to its appropriate carbon atom but is moved from an upper into a lower—or the reverse—plane of the carbon unit.

The models serve to bring out relationships which are patent to the chemist but not hitherto quantified, particularly in connection with the residual affinities shown by compounds generally. The higher paraffins and fatty acids are solid compounds, maybe of high melting point. It has always been difficult to account for this fact. In the model of a paraffin, the carbon skeleton is a two-layered structure like that of benzene; but whereas, in benzene, the carbon units rest upon "terfaces," in the paraffin the chain rests upon a succession of simple dodecahedral faces: the carbon units are, in fact, skewed. The hydrogen units are arranged in pairs on either side of the chain, therefore *not* at the tetrahedral angle; again, the affinities are exercised in two planes, those of the single carbon atom. In consequence, although each carbon affinity is engaged, it is but "partly covered or spoilt" and there is a considerable uncovered carbon

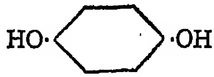
surface. When the unit models are superposed or conjoined these surfaces come into apposition, thus typifying the exertion of what, for want of a better expression, may be termed residual affinity. It is impossible, using such models, to typify carbon atoms as united by more than single "full" affinities. Only two forms of union seem possible, one that described, characteristic of paraffin and benzene; the other less complete in one sense, though it is such as to affect and "spoil" two affinities of each atom.

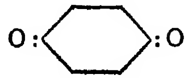
In the paraffins, three dodecahedra in each carbon unit are concerned in the single union. In the second geometrically possible mode of union, the jaws as it were of two atoms are interlocked—the result is that only two dodecahedra of the one are in contact with two of the other; the dodecahedra, however, do not belong to one "affinity face" as in the paraffin but to two. The model does indeed typify the eminently unsaturated condition of the ethenoids. In the acetenes, the third affinity of each of two carbon atoms is frankly to be regarded as unsatisfied, if the model be in any way a representation of the actual conditions. Whatever their ultimate value in connection with crystalline forms, such solid geometric models are undoubtedly bound to prove of great importance in the study of structure; their use, however, would seem to entail the use of a "geometric sense" but little developed hitherto. (For reproductions of the models, see Introduction.)

Colour

Whatever be the nature of the ethenoid form of union, it is the cause especially of marked optical peculiarities and in many cases of visible *Colour*. It is almost possible to assert that coloured compounds are all of one type—all *Quinonoid*. Quinone is a benzene derivative, formed by the removal of the two hydrogen atoms from the two

hydroxyl groups in paradihydroxybenzene (the photographer's hydroquinone) or quinol





The white quinol becomes yellow. To mention other simpler cases, mercuric iodide, which is a yellow or red crystalline solid, is colourless in certain solutions. Probably it is present in these as the simple molecule HgI_2 and in the solid form as a complex $(HgI_2)_x$. Iodomethane and diodomethane, CH_3I and CH_2I_2, are colourless liquids; triodomethane (iodoform) is a yellow solid. In these iodo-compounds the appearance of colour is probably determined by the "residual affinity" of the iodine. It is uncertain whether or no the simple molecule of iodoform be coloured; perhaps it is not and the solid may be better formulated as

$$\begin{array}{ccc} & (CH) & \\ I & I & I \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ I & I & I \\ & (CH) & \end{array}$$

and the assumption made that the *three unsaturated* centres developed between the three iodine atoms cooperate to produce visible colour. If so, a sufficient number of simple molecules of mercuric iodide may be supposed to associate to give at least three unsaturated ethenoid centres. The faint blue colour of liquid oxygen may well be due to the association of several molecules in a complex system.

The three centres in quinone are conceivably the phene nucleus itself plus the two unsaturated CO groups. It is, however, possible that the simple quinone molecules are associated—through the CO group—and that the

origin of the colour is in part extra-molecular. This is certainly true of a number of compounds in which colour is apparent. When the number of unsaturated centres is increased, the colour is intensified and almost reaches black. The blackness of charcoals is perhaps to be explained in this way: probably these and graphite are highly complex molecules in which carbon is present not in one form as in diamond but as ethenoid carbon, together with phenoid and paraffinoid. It is possible that it will ultimately be found that there is but one form of carbon—diamond—and that the supposed allotropes contain a very small proportion of hydrogen—that they are complex hydrocarbons, in fact.

Chemistry of Carbon Compounds

Organic chemistry, so-called, now a vast science, including hundreds of thousands of compounds, is entirely built upon the carbon foundations which have been described : the paraffinic and the benzenoid, the one open, the other a closed system. Infinite as is the variety of compounds, they are nearly all formed from the hydrocarbons by the introduction of oxygen (in relatively few cases, sulphur) or nitrogen, sometimes both, in place of one or more atoms of hydrogen. No two compounds are alike and yet, within families, the resemblances are close. At bottom, the power of the carbon atom to combine with the carbon atom almost indefinitely is the reason why so many carbon compounds are possible. No other element appeals and clings to itself in the same way. No other element could well give rise to life. We are essentially creatures of carbon, using water as lubricant and oxygen as stimulant. Perhaps the greatest work before us is to interpret molecular structure and the functions of the materials made use of by the organism in terms of

solid geometry. We shall then begin to have feeling knowledge of ourselves.

To be a chemist, it is necessary to have full appreciation of the characteristics of the families that enter into the world of carbon and to be in close acquaintance with many of its individuals. It is a difficult but fascinating occupation : once engaged in, the proper spirit of wonder and reverence being developed, it will be found to be the forecourt to many mansions of marvellous beauty.

We can only deal with life as built upon life, but our knowledge of the materials upon which its images are graven and of the graving processes is already astounding. Yet we are only on the outermost fringe of the inquiry, the difficulty of the problems to be solved is clear only to those who are absorbed in the study. The beauty of the solutions already found is in many cases beyond description but to how few is this revealed ! The plant is the great builder. Beginning with the simplest materials, it raises these to levels at which they become available to the animal organism, whose constructive power is limited to the arrangement and incorporation, not of simple bricks such as are handled by the plant but of larger units previously fashioned by the plant. Plant, in turn, is dependent upon soil, as well as upon sun. We are indeed of the earth, earthy, whilst children of the sun.

Plant Activities

Falstaff, in his day, could well say, "The World is mine oyster, which I with sword will open" : such was the method of old. To-day, we work with knowledge and hope to have done with swords—for a time, at least ; the more, the more we use our knowledge. Our cry may be, "The world is one great gasholder, whose holding we with our lungs devour." As the rays of the rising sun

strike the earth, they enter upon their daily task of keeping the holder filled, whilst its contents are constantly consumed by the plant and animal alike, chiefly by the latter. Our great luminary has been thus engaged throughout time, and much of his energy has been funded for us in ways and forms of which we take too little cognisance. We dispute much over coal and oil but take scant notice of oxygen—without which they would be worthless and life impossible : yet we have no full understanding of the ways of that oxygen, we pay little heed indeed to its marvellous power.

The initial act, on the part of the plant, is the absorption of carbon dioxide—present in the atmosphere in the minute proportion of only about three parts in ten thousand. Under some conditions, where much organic matter is undergoing decay, more may be present and, there is much evidence that growth is more rapid when the concentration is above the normal. It is beyond question that oxygen is evolved, in proportion to the amount of carbon dioxide assimilated, as if action took place in the sense of the equation :—

$$CO_2 + OH_2 = COH_2 + O_2$$

that is to say, as if the final oxidation product of carbon had been lifted back and up two steps towards methane, CH_4. No one doubts the explanation, although the compound COH_2, formaldehyde, has never been shown to be present in the plant cell by means which preclude the idea that it has not been developed in the course of testing. Chemists generally accept the explanation, because it appears to be the only one that will satisfy the conditions of the problem, the visible products of assimilation being such that not only may their production be accounted for by assuming that "formaldehyde" is their progenitor but it is scarcely possible to suppose

that they are produced in any other way. Moreover, formaldehyde, in the guise of $CH_2(OH)_2$, its hydrol, is a compound of intense chemical activity and it is not to be supposed that it could accumulate in the vegetable cell.

This is not to say that we know precisely how the aldehyde is produced: we do not. Still, it is already proved that assimilation only takes place under the influence of light absorbed by the chlorophyll, in the red region of the visible spectrum. The process may, therefore, be regarded as an electrolysis—every chemical interaction, be it remembered, is an electrolysis—effected by light, in which water is electrolysed in circuit with carbonic acid, this latter being eventually reduced to the aldehyde, whilst the complementary product, perhydrone, is resolved into oxygen and water. Written empirically, the change may be expressed by the equation:—

$$CO(OH)_2 + 4(H.....OH) = COH_2 + 2OH_2 + 2HO{\cdot}OH$$

If so, the oxygen in reality is derived from water. The carbonic acid primarily serves the purpose of taking charge of the hydrogen which must be separated from hydrone to produce oxygen. The reduction product alone is of special (constructive) value to the plant; oxygen is returned to the atmosphere, in place of the carbon dioxide removed, sooner or later to play a destructive part but, in so doing, to let loose and pass on the energy derived from the sun. Much energy from the sun is also stored in the formaldehyde. The quantity of solid formaldehyde corresponding with the formula (CH_2O) expressed in grammes (30 grammes, since $C=12$, $H=1$, $O=16$), when burnt, gives rise to 122,880 gramme-calories, that is to say, sufficient heat to raise the temperature of this number of grammes of water 1° Centigrade. The contained carbon and hydrogen, if burnt alone, the

former in the form of charcoal-carbon, would furnish 96,960+68,360 gramme-calories. Formaldehyde, therefore, has within itself about three-fourths of the energy of the contained carbon and hydrogen. It is thus shown how great a work is done by the sun.

Chlorophyll

As chlorophyll is concerned and solar energy made operative through its absorptive action, it is necessary to assume that the electrolytic circuit is one in which the chlorophyll is included. Chlorophyll is a nitrogenous compound of great complexity and one of the most remarkable known. It is closely related to blood haematin but, whilst iron is a characteristic constituent of the latter, magnesium is similarly the outstanding constituent of chlorophyll. Haematin, as haemoglobin, has the power of combining with oxygen; it combines even more firmly with carbonic oxide (CO) but not with carbon dioxide. Chlorophyll shows no such associative tendencies, yet to explain its action we are almost forced to assume that it can combine, at least loosely, with carbonic acid. It has been surmised—it is only a surmise—that the association is through the magnesium atom, that this becomes partially unclasped through the action of carbonic acid, so that an acid carbonate, $XO{\cdot}CO(OH)$, is formed. That such a carbonate might undergo reduction, in an electrolytic circuit, to the *formaldehydrol* derivative $X{\cdot}O{\cdot}CH_2(OH)$ is possible, to say the least; indeed, it is probable that it would. Still, as chlorophyll is a pyrole derivative and laden with nitrogen, it is conceivable that it may act basically, apart from its magnesium. More it is impossible to say: the problem is one, however, which should not be put aside.

Whatever be the precise nature of the operation where-

by formaldehydrol is produced, we have no reason at present to believe that it is otherwise than the sole immediate product of solar activity. In like manner it is at least probable that the higher carbohydrates which are formed by its condensation are the only compounds which are in the direct line of succession as solar products; of these, be it said, cellulose is the only one which is of structural value as cuticular material. The plant cell is a laboratory of wondrous activity. Within it are built the great variety of products which form the plant—quietly, without perceptible ostentation, at ordinary temperatures, often in the dark, underground, as in the potato tuber. Thus far we have been unable to prepare starch or even cane sugar. To imitate the operations of nature we need most elaborate and expensive appliances and often work at high temperatures and pressures. When we think of the way in which nitrogen and hydrogen are converted into ammonia in the root nodules of leguminous plants, apparently by a minute organism living an imprisoned, airless life—when we contrast this with the great array of pumps, compression vessels and many other mechanical appliances used in the factory to the same end, we may indeed hang down our heads in very shame at our ignorance of all that is fundamental in the minute operations of nature. To pour such material, so made, as fertiliser upon the soil, when the humble bacterium by which it is populated can do the work on the spot, if only properly encouraged, may some day come to be regarded as soil sacrilege.

Formation of Carbohydrates

Under laboratory conditions, formaldehydrol rapidly undergoes change in presence of a mere trace of an alkali. The product is a complex mixture and has never been

successfully unravelled : it contains *fructose*, however, on of the components of cane sugar. The process of chang is only partly understood and is in doubt so far as th precise nature and succession of the changes betwee: aldehydrol and sugar is concerned but is, in essence, *condensation* and typical of a great number of up-grad changes which take place under natural conditions. I may therefore well be discussed at length. Perhaps *thre* molecules interact simultaneously thus :

$$\begin{array}{lcl} \mathrm{HO{\cdot}CHH{\cdot}OH} & & \mathrm{CHH{\cdot}OH} \\ & & \quad| \\ \mathrm{HO{\cdot}CHH{\cdot}OH} & = & \mathrm{CH{\cdot}OH} + 2\mathrm{OH_2} \\ & & \quad| \\ \mathrm{HCH(OH)_2} & & \mathrm{CH(OH)_2} \end{array}$$

This product, glyceraldose (hydrol), the aldehyde o: glycerol, at once suffers internal change and is convertec into the corresponding isomeric ketone—glyceroketos((hydrol),

$$\begin{array}{lclcl} \mathrm{CH_2{\cdot}OH} & & \mathrm{CH_2{\cdot}OH} & & \mathrm{CH_2{\cdot}OH} \\ | & & | & & | \\ \mathrm{CH{\cdot}OH} & \leftrightarrows & \mathrm{C{\cdot}OH} + \mathrm{OH_2} & \rightleftarrows & \mathrm{C(OH)_2} \\ | & & () & & | \\ \mathrm{CH{\cdot}OH{\cdot}OH} & & \mathrm{CH{\cdot}OH} & & \mathrm{CH_2{\cdot}OH} \end{array}$$

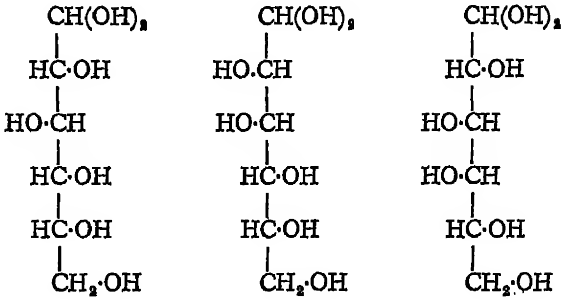
These triplets interact, in pairs, in various ways. The production of fructose may conceivably take place in the following manner, by the condensation of glyceraldose and glyceroketose,

$$\begin{array}{llcll} & \mathrm{CH_2{\cdot}OH} & & \mathrm{CH_2{\cdot}OH} & \\ \text{Glyceraldose} & | & & | & \\ \text{(hydrol)} & \mathrm{CH{\cdot}OH} & & \mathrm{CH{\cdot}OH} & \\ & | & & | & \\ & \mathrm{CH(OH)_2} & & \mathrm{CH{\cdot}OH} & \\ & & = & | & +\mathrm{OH_2} \\ & \mathrm{CH_2{\cdot}OH} & & \mathrm{CH{\cdot}OH} & \\ \text{Glyceroketose} & | & & | & \\ \text{(hydrol)} & \mathrm{C(OH)_2} & & \mathrm{C(OH)_2} & \\ & | & & | & \\ & \mathrm{CH_2{\cdot}OH} & & \mathrm{CH_2{\cdot}OH} & \end{array}$$

The production of glucose may be represented as involving the interaction of two molecules of glyceraldose (hydrol),

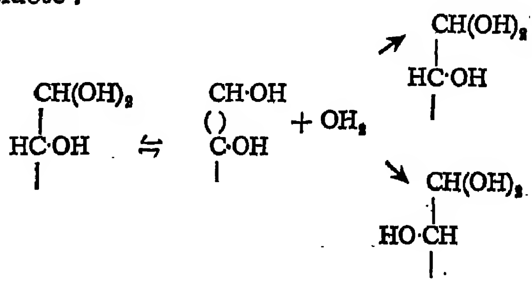
$$
\begin{array}{lcll}
CH_2{\cdot}OH & & CH_2{\cdot}OH & \\
| & & | & \\
CH{\cdot}OH & & CH{\cdot}OH & \\
| & & | & \\
CH(OH)_2 & & CH{\cdot}OH & \\
 & = & | & + OH_2 \\
CH_2{\cdot}OH & & CH{\cdot}OH & \\
| & & | & \\
CH{\cdot}OH & & CH{\cdot}OH & \\
| & & | & \\
CH(OH)_2 & & CH(OH)_2 &
\end{array}
$$

The formulae here used are mere paper-written expressions and not intended to indicate actual structure —they do so only broadly. It will be noted that in the glucose formula four of the carbon atoms and in the fructose formula three each carry four different radicles; the two sugars are therefore structurally asymmetric materials and should be optically active. The natural products are, whilst the compounds produced in the laboratory are not, optically active, simply because the latter are mixtures of compounds of opposite optical activity. In point of fact, variations in internal structure are brought about by merely varying the relative position of the (OH) groups in the CH(OH) member of the structure. In all, 16 isomeric glucoses are possible: these form two sets of eight, corresponding terms in which are of equal, opposite structure and optical activity. The three isomeric natural sugars, glucose, mannose and galactose, are represented by the following expressions, showing the relative arrangement of the hydroxyl groups in the asymmetric members:



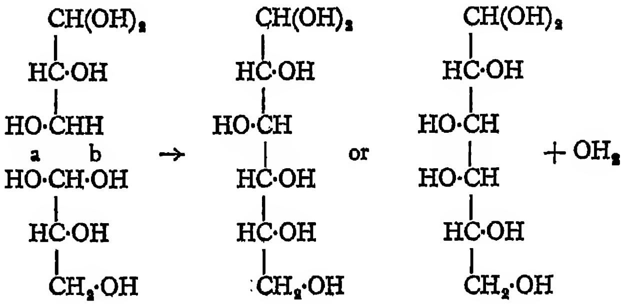
Glucose Mannose Galactose

The structural relationship between these three forms is of a very simple character. If the position of the OH group in glucose on the right of the formula attached to the second carbon above from the top, be reversed, the formula becomes that of mannose. As a matter of fact, this change gradually takes place, to a slight extent, when merely a little alkali is added to a solution of glucose. The process is probably that already pictured of glyceraldose:



The peculiar ethenoid linkage developed by withdrawal of hydrone from the aldehydrol may be broken on either side and the OH may be restored, either in its original position or reversed. The change from glucose to galactose may be pictured in an equally simple manner. Assuming either that the glucose be first resolved into

two molecules of glyceraldose or that the two sugars be each formed directly from two such molecules,



either glucose will be reproduced or galactose will be formed, according as either the OH group marked (a) or that marked (b) be removed in the extruded molecule of hydrone. The position of only one of the OH groups is changed. These are not mere matters of speculation: such changes actually happen, before our eyes, in the laboratory.

Optical Activity

When compounds are produced artificially which are potentially (by structure) optically active, the two optically active forms, of equal opposite activity, are both produced usually in equal amounts, so that the product is optically inactive. The chances of the action going this way or that, unless specially directed, are equal. In nature, all such compounds are produced initially in the one optically active form—nature, as it were, is one-handed and wears but a single glove. Nature's factory only turns out gloves for, let us say, right-handed wearers. When both appear, as happens in a few cases, there is reason to believe that a change has taken place after nature has ceased to exercise her directive influence.

Of all the facts disclosed by the study of natural products, this restriction placed upon herself by nature is the most remarkable. The discovery is the outcome of Pasteur's initial, most wonderful, prime discovery that racemic acid, an optically inactive product got from wine-lees, could be resolved into equal parts of ordinary right-handed tartaric acid and of a left-handed twin thereof. It is an important consequence of this generalisation that natural chemistry is, in a sense, simpler than laboratory chemistry.

How is the natural process by which a sugar such as glucose is formed to be pictured? It is as if the formaldehydrol molecules were threads the two ends of which are passed through contiguous holes in a piece of canvas. A number of such threads, being thus arranged, may obviously be tied together at the back of the canvas in various ways and the loose ends then clipped off, leaving distinctive elements of the thread arranged in some pattern on the front. Such a pattern might conceivably be produced by lowering upon the canvas a plate with holes through which the threads could be drawn only at certain points and thereby determining the ways in which they could be tied together. In the plant, more probably, the reverse influence may be at work. The pattern may exist in the plant in the form of the substance to be produced: a sugar molecule may conceivably be formed upon what is practically a sugar molecule; that of starch upon a starch molecule; hence the apparently immediate appearance of starch. If such be the case, we can understand the formaldehydrol molecules becoming properly placed upon the guiding molecule, particularly in virtue of the attraction exercised by the (OH) groups in this upon those in the corresponding positions in the formaldehydrol molecules, leaving others in the position of loose ends to be snipped off at the right

moment. When models of benzene derivatives such as have been described are packed together to form the crystal, more often than not they form a stepped pavement, as it were, alternate units being at one or other of two levels. Starch may well be so constructed and it is possible to picture a series of formaldehydrol molecules dropping into place, in orderly arrangement, upon such a platform, ready to be tied together.

Enzyme Action

How is the tying done? it may be asked. The operation is so easily effected in the laboratory that no special mechanism may be required. A trace of alkali or even acid may suffice. On the other hand, there is much evidence that, under natural conditions, the more complex carbohydrates are usually broken down through the agency of special agents, known as *enzymes*; therefore, it is at least probable that they are formed by the converse process, as such interactions are known, in many cases, to be reversible and should be in all, though the point of equilibrium may be so near to the one side that the change may appear to be unilateral. The general equation of enzymic hydrolysis may in fact be written thus:

$$A'B' + \varepsilon\delta\kappa\, OH_2 \leftrightharpoons A'(H) + B'(OH) + \varepsilon\delta\kappa$$

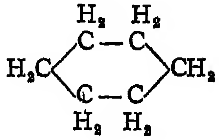
The difficulty that arises in the attempt to apply this generalisation is that the necessary agent is not always obvious. Thus, it is known that the constituents of cane sugar, glucose and fructose, both travel down in large quantity from the leaf to the bulb and there become associated as cane sugar: the bulb, however, does not contain the enzyme *invertase*, although this is present in the growing leaf. The enzyme appears to travel down into

the bulb only when the growing period sets in and the store in the bulb is utilised in forming a new season's growth.

A further structural peculiarity in the sugars may now be referred to, as it is one that must be taken into account in discussing their formation. In the normal paraffins, as explained, the carbon atoms are simply arranged in a series or row, atomic centres meeting at an angle of 109°28′, at successive corners of a zigzag. In the phenes, the angle of the approach of the carbon atoms may be supposed to be the same but they are arranged in compact closed systems—in sheets of more or less frequently repeated hexagons. The sugars are also peculiar. Glucose is derived from the alcohol mannitol, which, in turn, is derived from the paraffin hexane, by the displacement of six of the hydrogen atoms, one from each carbon atom, by the radicle (OH). Glucose bears to mannitol the relation of aldehyde to alcohol but the aldehydic properties are so feebly displayed that chemists have always dubbed it an aldehyde with hesitation. One peculiarity of glucose is the ease with which it is etherified. When it is dissolved in methylic alcohol and the solution is slightly acidified with hydrogen chloride, it is soon converted into a mixture of products but chiefly into two isomeric monomethylic derivatives, α- and β-methoglucoside, $C_6H_{11}O_5(OCH_3)$. In neither of these is the slightest trace of aldehydic behaviour to be found. A (third) γ-glucoside isomeric with the α and β forms has also been isolated which is chemically a far more active substance. A solution of glucose appears to contain but a minute proportion at most of this γ form and consists mainly of the α and β forms in equilibrium.

Chemists are now of opinion that the glucoses and these glucosides are closed systems, analogous to that of phene (benzene) but saturated. Phene itself may be converted

into a saturated system, C_6H_{12} (hexahydrobenzene or hexamethylene), which is scarcely distinguishable chemically from the paraffin hexane:

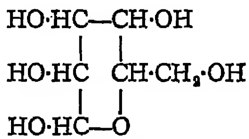


A hexhydric alcohol, $C_6H_6(OH)_6$, derived from this hydrocarbon, is a natural product. Being closed systems derived from phene but saturated like methane and its substitution derivatives, such compounds are conveniently spoken of as *phanes*.

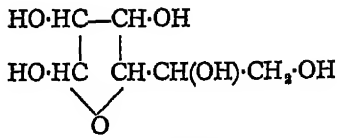
Geometric Structure of Sugars

A simple and rational formal expression of the peculiar behaviour of glucose and especially of the methoglucosides is given if it be assumed that they are *oxophanes*, phanes in which several atoms of carbon are linked in a closed system by means of an oxygen atom. If so, one end of the paraffinic chain of mannitol becomes, as it were, soldered to a link along the chain, when, by hydroxylation, the terminal carbon atom is converted into the aldehydrol and a molecule of hydrone is thereupon withdrawn from the compound. To what "link" down the chain is the terminal atom thus united? The problem has given rise to a large amount of work and an equal amount of speculation, extending over years—we are not yet satisfied that the solution is in our hands. The most probable "interpretation" of the character of glucose and the glucosides, however, is now thought to be that given by the assumption that they are *phanoids*: that α- and β-glucose and the corresponding glucosides—are hexaphanes

(hexoxophanes) and γ-glucose and the γ glucosides pentaphanes (pentoxophanes).

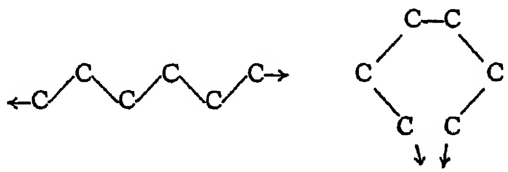


α- and β-glucose



γ-glucose

Assuming such to be the case, what is mannitol—is it truly paraffinic or is it potentially *phanoid* ?



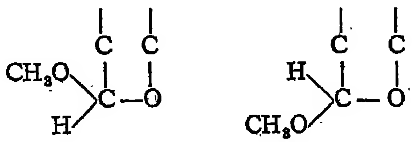
When hexane is gradually hydroxylised, does the carbon chain remain, like a billiard cue, essentially a straight one or does it bend ? If the latter, when is the "screw" put on ? This is an inquiry into the art of the chemical stevedore which the X-ray analysts must help to solve. Whenever it occurs, the "bending" is doubtless a necessary consequence of the loading of the molecule with oxygen and the attraction which oxygen has for oxygen. It may be added that although the formulae are written as "rings": actually in the model the carbon atoms are close packed either in clumps or in closed systems. Four and five may be united by an atom of oxygen but the minimum number of carbon atoms in a normal closed system is possibly six.

Returning now to the consideration of the manner in which carbohydrates are formed in the plant, it may be pointed out that although glucose is the fundamental carbohydrate unit, the opinion prevails, at the moment,

that cane sugar, not glucose, is the primary product; starch may also be a primary product but, as it is scarcely present in the leaves of monocotyledons, it is no longer supposed, as it once was, that this is *the* one and only initial product of assimilation. In any case, the carbohydrates should be regarded as immediate primary products of solar activity, if built up, as such, from carbonic acid, as this is reduced under the immediate influence of chlorophyll. If formed from formaldehydrol first set free in the cell fluid they are but secondary products. The fact remains that in some plants the chloroplasts become laden with starch; in others, in which cane sugar rather than starch seems to function as reserve material, they do not. Yet in these latter, if the concentration of the sugar within the leaf be raised by dipping the cut end into a strong solution of sugar, their chloroplasts equally become laden with starch. Apparently, in monocotyledons, the conditions of concentration are not normally those required for the production of starch; or maybe they are such that the starch is no sooner formed than it is hydrolysed and passes out as a lower sugar. The more probable explanation seems to be that the units assembled upon the template are tied together perhaps only in pairs and that these float away. Dilution would operate against the continued linking up of molecules.

The essential carbohydrates are certainly glucose and fructose, cane sugar, starch, inulin and cellulose. Whilst cane sugar is compounded of glucose and fructose, inulin is composed of fructose, starch and cellulose being formed of glucose alone. The units are differently arranged and in different numbers in the higher sugars, in unknown numbers in inulin, starch and cellulose. The difficulty of dealing with starch is enhanced by recent discoveries: that what is commonly called starch is not a single substance and that, apparently, a single layer in a granule

may be a mixture of "starches." Though starch and cellulose are ultimately resolved by hydrolysis into the same glucose, diverse products are obtained on the way—the one yielding *maltose*, the other *cellobiose*, both isomerides of cane sugar. The relation of these three, however, is simple, as fructose, which is associated with glucose in cane sugar, is but glucose slightly modified and the other two are perhaps respectively α and β glucosides corresponding to the α- and β-methoglucosides already considered, the difference between these being simply that the methyl group is attached in one or other of the two possible positions to the carbon atom next to the oxygen link in the oxophane.



There is still much uncertainty on these points. Taking all the peculiarities into account, which are thus apparent, it is clear that the formation of sugar is a directed process from the beginning—that the sugars are all, as it were, formed against templates or patterns present in the plant cell. Whether formaldehydrol be produced and sent into circulation or whether it be directly laid down to one or other carbohydrate, matters little—the primary elements are ultimately arranged and linked up in definite ways. The pattern cannot well be other than the thing itself. Cane sugar, however, being an intensely soluble material, cannot be thought of as acting as such. Yet it is not difficult to picture molecules of cane sugar being built into the protoplasmic structure of the chloroplast and the assembly, at such centres, either of formaldehyde or of glycerose molecules, which thereupon interact and give

rise to cane sugar itself. But how? Some mechanism must be imagined to tie the threads (OH+OH) and cut off the spare ends (as OH_2) in the way previously considered. Formaldehydrol and the sugars are in themselves inert—they are not electrolytes. They must be made into electrolytic conductors, by means of acid or alkali, before they will act together or give way to attack. We know that, in the fermentation process, glucose is first associated with a phosphate. We know that in the plant phosphate plays a determining part. It is not going far to assume that phosphate comes into play in the formation of carbohydrate: how exactly, whether in the shape of a floating mechanism—such as an enzyme—or as a molecule held in the protoplasmic complex, much as the crane is now placed on a building in course of erection, it is impossible to say. That the phenomena are of such an order would seem to be highly probable.

Away from the leaf, leucoplasts are met with in which transitory starch is often found, so that the enzymic mechanisms would seem to be widely distributed.

These mechanisms are clearly things apart—little factories in which special operations are carried on. For example, in sorrel, which is a strongly acid plant, the chloroplasts in the leaf are to be seen tucked away, as it were, in corners of the cells and are clearly independent of the acid in the fluid in which they float, their lining membrane being impervious to acid: if this membrane be broken down by exposing the leaf to chloroform, at once the chlorophyll is changed in appearance. Normally, it would seem, sugar must be able to pass out, although acid cannot pass in—but sugar is not an electrolyte. Such observations are the clearest possible evidence that the reduction of carbonic acid takes place within the chloroplast: that the formation of carbohydrate is effected under its influence would also seem to be open to little

doubt. In the starch granule, there seem even to be traces left, between "the starch molecules," of the erecting mechanism. We have yet to learn whether the silica in the cereal stem be not such a survival, not a mere strengthening inclusion.

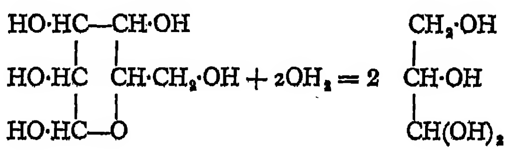
Constructive Metabolism

Having made sugar, the plant proceeds to use it in its many wondrous feats of constructive metabolism. The micro-organism—the yeasts and all unicellular organisms—we know is able from sugar alone as organic pabulum, with the aid of a few mineral salts, to reproduce itself to an unlimited extent. Raulin's nutrient solution, much used by Pasteur as a medium for growing mould organisms, was composed as follows:—

Water	1,500	Carbonate of Magnesia	0·4
Sugar candy	70	Sulphate of Ammonia	0·25
Tartaric acid	4	Sulphate of Zinc	0·07
Nitrate of Ammonia	4	Sulphate of Iron	0·07
Phosphate of Ammonia	0·6	Silicate of Potassium	0·07
Carbonate of Potassium	0·6		

Apart from the singular power, possessed by the higher plants, with the aid of chlorophyll, of reducing carbonic acid and of meeting the many requirements of cells of different orders, the chemical functions of unicellular and multicellular organisms would seem to be similar. When the compounds other than sugar present in the plant and more particularly in the animal, in which sugars play a very minor constructive part, serving mainly as fuel, are considered, it is obvious that they all contain very much smaller proportions of oxygen than the sugars. The life of the plant is essentially a reductive process—as indeed it is in the beginning, as the evolution of oxygen

is but an accident of the reduction of carbonic acid by means of hydrogen derived from hydrone, the oxygen being cast aside as a by-product, of no account to the plant. We have to explain the constant withdrawal of oxygen. Only one agent is at disposal for the purpose—that used in the first act: hydrone. We have to account for the disposal of its oxygen—without further direct assistance from the sun. Inasmuch, however, as starch contains about half the energy the carbon and hydrogen that are in it would furnish if burnt alone, the plant actually continues to work even in the dark with energy derived from the sun, the more as it also makes use of oxygen. Whatever the carbohydrate reserve material, it is brought down to a hexose, chiefly glucose, for use. Much of the experimental evidence seems to be in favour of the view that glucose first undergoes resolution, by hydrolysis, into two molecules of glycerose. This, at least, seems to be the first stage in alcoholic fermentation under the influence of the complex enzymic mechanism in yeast (zymase).



It is noteworthy that the presence of phosphate is essential and that, in a preliminary stage, the phosphate and hexose interact. The argument has already been put forward but may be repeated, that, in the converse process, in the plant, phosphate is also operative and that this is an indication of at least one reason why phosphate is essential for plant growth. The reason why phosphate is essential is perhaps not far to seek. Glucose by itself, in aqueous solution, is not an electrolyte and, therefore,

should not be open to attack—by the introduction of an acidic radicle into its structure, it becomes an electrolyte and can therefore be included in a circuit of change.

The two isomeric trioses, glyceraldose and glycero-ketose, like the isomeric hexoses, glucose and fructose are mutually interconvertible—under the influence of a trace of alkali. The process is probably of the following order :—

$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH{\cdot}OH{\cdot}OH \end{array} \quad \leftrightharpoons \quad \begin{array}{l} CH_2{\cdot}OH \\ | \\ C{\cdot}OH + OH_2 \\ () \\ CH{\cdot}OH \end{array} \quad \leftrightharpoons \quad \begin{array}{l} CH_2{\cdot}OH \\ | \\ C(OH)_2 \\ | \\ CH_2{\cdot}OH \end{array}$$

This change takes place rapidly and when equilibrium is attained both compounds are present in large proportions. Glucose is only very partially changed reversively into the ketose fructose by a similar isomeric change. In the fermentation process, this type of change is carried a stage farther, apparently under enzymic influence, though it can be effected with the aid of alkali :—

$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH(OH)_2 \end{array} \quad \leftrightharpoons \quad \begin{array}{l} CH_2 \\ () \\ C{\cdot}OH + OH_2 \\ | \\ CH(OH)_2 \end{array} \quad \leftrightharpoons \quad \begin{array}{l} CH_3 \\ | \\ C(OH)_2 \\ | \\ CH(OH)_2 \end{array}$$

The compound thus produced (pyruvic aldehydrol) is eminently oxidisable and easily oxidised to pyruvic acid—$CH_3{\cdot}CO{\cdot}CO(OH)$. It is thought that this acid is formed and, by hydrolysis, resolved into aldehyde and carbonic acid—

$$CH_3{\cdot}CO{\cdot}CO(OH) + OH_2 = CH_3{\cdot}COH + CO_2 + OH_2.$$

It is known that yeast contains a peculiar ezyme, *carboxylase*, which will effect this change. Also, that if the

fermentation be carried out in presence of a sulphite, aldehyde may be obtained in large quantity, in place of ethylic alcohol. Further, if the liquid be maintained alkaline, much of the glyceraldose (also the ketose) escapes oxidation and is reduced to glycerol—which is but a very minor product of fermentation under ordinary conditions. It is thus seen how the glycerol of fats may be produced.

The production of alcohol in the fermentation process may be regarded as one in which two separate molecules are concerned and *reciprocally hydrolysed in circuit*, the one being hydrogenised, the other hydroxylised :—

$$CH_3{\cdot}CH(OH)_2 + \begin{matrix} H & \cdots & OH \\ H & \cdots & OH \end{matrix} + CH_3{\cdot}CH(OH)_2 =$$
$$CH_3{\cdot}CH_2(OH) + OH_2 + \ \ldots\ + OH_2 + CH_3{\cdot}C(OH)_3$$

The ordinary hydrolysis of cane sugar may be regarded as a change of this order but one in which the two separate halves of the molecule are reciprocally affected, the one being hydrogenised, the other hydroxylised.

To bring the processes into more complete agreement, proof is required of some mechanism in the fermentative process whereby the two aldehyde molecules are assembled in circuit with hydrone. Possibly, only suitable determining conditions of acidity and concentration are necessary —no special catalyst. (See note, p. 116.)

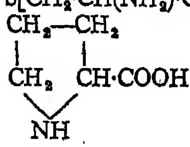
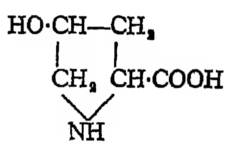
It is possible to ferment sugar in a variety of ways. Thus, from it may be produced normal butylic alcohol and acetone, instead of ethylic alcohol. It is not difficult to explain the process. Aldehyde is easily condensed in the following manner :

$$CH_3{\cdot}CH(OH)OH + CH_3{\cdot}CH(OH)_2 =$$
$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH)_2 + OH_2$$

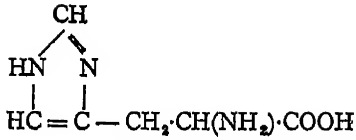
This compound is convertible, by direct reduction, into

normal butylic alcohol, whilst on oxidation it gives acetoacetic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OH$, which is easily resolved into acetone and carbonic acid. It is not difficult to visualise the formation of complex fatty acids as a consequence of continued condensation and reduction, accompanied by the necessary amount of hydroxylation to form the necessary hydrogen.

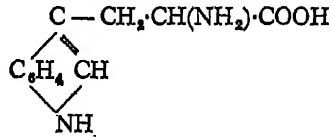
Proteins.—The origin of proteins is to be sought in this same direction. It is known that these are but collections of simple molecules, formed by condensation of molecule upon molecule, a great variety of molecules being thus linked together. The units range from aminoacetic acid, $CH_2(NH_2) \cdot CO \cdot OH$ upwards, as shown in the following table.

Glycine	$CH_2(NH_2) \cdot COOH$
Alanine	$CH_3 \cdot CH(NH_2) \cdot COOH$
Valine	$(CH_3)_2CH \cdot CH(NH_2) \cdot COOH$
Leucine	$(CH_3)_2CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Isoleucine	$(CH_3)(C_2H_5)CH \cdot CH(NH_2) \cdot COOH$
Serine	$CH_2(OH) \cdot CH(NH_2) \cdot COOH$
Lysine	$H_2N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Arginine	$HN : C(NH_2) \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2CH(NH_2) \cdot COOH$
Phenylalanine	$C_6H_5 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Tyrosine	$HO \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Aspartic acid	$HOOC \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Glutamic acid	$HOOC \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
Hydroxyglutamic acid	$HOOC \cdot CH_2 \cdot CH(OH) \cdot CH(NH_2) \cdot COOH$
Cystine	$S[CH_2 \cdot CH(NH_2) \cdot COOH]_2$
Proline	
Hydroxyproline	

Histidine



Tryptophane



The production of such amino-acids is to be accounted for without much difficulty, bearing in mind what is said above of the manner in which hydroxy-(keto) acids, such as pyruvic acid, are formed in the fermentation process and the readiness with which these are attacked by ammonia :

$$CH_3{\cdot}C(OH)_2{\cdot}CO{\cdot}OH + NH_3 = CH_3{\cdot}C(OH)(NH_2){\cdot}CO{\cdot}OH + H_2O$$

Such an acid, on reduction, would be converted into amino-propionic acid or alanine, a constituent of many proteins. Aminoacetic acid (glycine) is conceivably derived in a similar way from glyoxylic acid, $CH(OH)_2{\cdot}CO{\cdot}OH$, this being one of the normal oxidation products of glycerose.

The only series of compounds present in plants of which the origin is at present obscure are the phenoid derivatives, phenylalanine, tryptophane and tyrosine, which are present in most of the proteins. Broadly speaking, however, it is clear that they are formed from simple materials by condensation processes such as those explained.

As to the structure of the proteins, we have no conception, at present, whether their molecules are long-drawn-out systems like those of the fatty acids or compressed like the saccharons. The latter is the more probable. Regarding them as forming sheets of a pavement-like character, it is possible to conceive the arrangement of

the several units upon pre-existent molecules of the protein and the consequent determination of the order of arrangement. Without some such interpretation, it is impossible to explain the persistence of particular proteins in particular materials of either animal or vegetable origin.

Nitrogen Absorption

Plants of non-leguminous orders apparently derive their nitrogen, at least for the most part, from ammonia in the soil. Nitrates, we know, pass into the plant and may even be stored in the cells in considerable amount. Nitrates are not easily reduced, however, and proof has yet to be given that they are directly utilised by the plant. The remarkable direct absorption of nitrogen by organisms in the soil and by others living in the nodular growths found especially upon the roots of leguminous plants is in no way understood at present. Probably, it is to be associated with the occurrence of intense oxidative changes, which make hydrogen disposable at a high potential. The absorption of so inert a material appears to be less remarkable than it did, now that vast quantities of ammonia are produced by the direct interaction of hydrogen and nitrogen under the influence of a catalyst —but this is effected at a high temperature and under a high pressure, not within the cold soil. Strangely enough, the production of ammonia by direct reduction of nitrogen has never yet been observed under ordinary simple laboratory conditions.

Methylic Alcohol

A reference may be interposed to modern synthetic methods of producing organic materials which may well put fermentation processes and natural sources into the shade. Methylic alcohol has long been produced as a

by-product in the manufacture of charcoal—formerly much used for gunpowder. Formaldehyde, which has been greatly in demand of late years, has been prepared by oxidising such alcohol. It has recently been shown that, in presence of a suitable catalyst (zinc oxide), under appropriate conditions of temperature and pressure, carbonic oxide and hydrogen readily interact and may be converted all but completely into methylic alcohol. At higher pressures the product is more complex and, by using appropriate catalysts, a whole series of paraffinic alcohols may be produced. Possibly, formaldehyde molecules are formed and brought into interaction and condensed, as they are in the plant, the product being at once reduced. Also carbides may intervene.

Oxidation

In the animal, oxidation is at the root of muscular activity. The extent to which it is effected as an independent process is not clear but the fats, at least, must be primarily oxidised to some extent before they are rendered available for the purposes of muscular activity. Oxygen is so essential to plant life that the gas must take part in its vital activity but it is in no way clear what special function oxygen subserves. Many organisms can live without air, the yeasts all do: oxygen becomes necessary, however, at the reproductive stage, though only in minimal amount. Aerobic organisms use up a large amount of oxygen. In the animal, oxygen is stored in haemoglobin as oxyhaemoglobin and thence passes into solution as required, a definite equilibrium being maintained between the oxygen within the red blood corpuscles and the solution without the cell. Oxyhaemoglobin itself, apparently, has no action as an oxidising agent. At root, the oxidation (hydroxylation) process in

plant and animal is alike in its nature, it may be supposed. Usually, if not always, a catalyst as well as a determinant is involved in the change—the oxidising catalysts are known generally as oxidases. These have been classed as enzymes but modern work is tending more and more to show that, though they may differ and be limited in their range of activity, they are not enzymes in the sense of being selective agents in some way structurally related to the compounds they affect. The enzymes, as a class, are apparently all hydrolytic agents; at least, it may be desirable to confine the use of the term to agents exercising this function alone.

Thanks to the refined work of Fletcher, Hill and Gowland Hopkins in particular, it is now clear that the act of muscular contraction derives its energy from an essentially enzymic process, akin to that of fermentation, whereby hexose (glucose) is converted into lactic acid, $CH_3{\cdot}CH(OH).CO{\cdot}OH$—only then does oxygen become directly operative. Apparently the lactic acid is merely hydroxylated and the product, $CH_3{\cdot}C(OH)_2{\cdot}CO{\cdot}OH$, for the most part rebuilt to hexose.

In this connection, it may be well to discuss more closely the phenomena of oxidation in general. It may be submitted that not only, as already stated, (1) is oxidation primarily, in so far as the oxidised compound is concerned, a process of hydroxylation but (2) that oxygen or whatever oxidising agent be used is active only indirectly—as depolariser and adjuvant in an electrolytic circuit. The oxidation of hydrogen has already been formulated from this point of view, thus:

$$\begin{array}{c} H \\ | \\ H \end{array} + \begin{array}{c} HO\ldots H \\ \\ HO\ldots H \end{array} + \begin{array}{c} O \\ | \\ O \end{array} = 2H_2O + HO{\cdot}OH$$

Whereas hydrogen and oxygen interact readily, at the surface of a platinum plate (in presence of the necessary

determinant), a mixture of carbonic oxide and oxygen not only remains unaffected at moderate temperatures but, if carbonic oxide be added to the mixture of oxygen and hydrogen, it actually inhibits their interaction under the influence of platinum.

Carbonic oxide and hydrogen have very nearly the same heats of combustion, that of hydrogen (to liquid water) being slightly above, that of carbonic oxide slightly below, 68,000 units. It may be suggested that 68,000 is a *limiting value* and that no interaction in which a less amount of energy is developed will take place directly—without an adjüvant or depolariser. This seems to be an immediate corollary to the view, that as the action is electrolytic the determinant is necessarily liquid and composed of water and a salt. Carbonic oxide should be incombustible in the absence of a depolariser, if this view hold good, as water must be electrolysed in the circuit of change.

The fact that it explodes when moist may be accounted for by the assumption that the spark or flame applied to the mixture causes the production or introduction of a slight amount of hydrogen, which is burnt along with it, a supply of hydrogen being kept up by a slight decomposition of water in the wave front as the explosion spreads. Prof. Bone has found that the mixture becomes less and less easily exploded, requiring the application of a greater and greater intensity of current to force a discharge across the sparking gap, as the drying is more and more complete. Using phosphoric anhydride as drying agent, a limit is reached but only after several months. Explosion ultimately takes place but only when a very powerful electromotive force is applied; it is attended with a most brilliant flash of light but the interaction is far from complete. What is the explanation of this behaviour? Maybe a sufficient amount of the

electrolytic determinant is expelled from the platinum wire electrodes by the discharge in the form of previously imprisoned hydrogen molecules and "spluttered" platinum motes. There is urgent need to consider problems of this kind, in view of the importance attached to the discharge of electricity through gases by physicists, who are paying no attention whatever to the purity of the materials and the possible variation in the system through which the discharge is passed.

Carbonic oxide is perhaps the most interesting of all oxidisable gases. It needs little drying to render it incombustible and its combustibility grows, as the amount of moisture present is increased, over a considerable range. The probable explanation of this behaviour is that it is hydroxylised, not as such but indirectly through the determinant which becomes associated with it. The compound $\mathrm{CO}\left<\begin{matrix}\mathrm{H}\\ \mathrm{OH}\end{matrix}\right.$, being of a very low order of stability, would necessarily be in very small proportion unless a considerable proportion of hydrone molecules were present. The condition is comparable with that of a *very weak* acid in solution.

The influence of hydrogen and of hydrocarbon, in promoting the combustion, when present together with the gas, may be ascribed to the initial formation of perhydrone from the hydrogen, which then functions as active depolariser in the carbonic oxide circuit.

$$\mathrm{CO}\left<\begin{matrix}\mathrm{H}\\ \mathrm{OH}\end{matrix}\right. + \begin{matrix}\mathrm{HO}:\ldots\mathrm{H}\\ \mathrm{HO}\ldots\mathrm{H}\end{matrix} + \begin{matrix}\mathrm{HO}\\ |\\ \mathrm{HO}\end{matrix} = \mathrm{CO}\left<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + \mathrm{OH_2} + \begin{matrix}\cdots\\ \\ \cdots\end{matrix} + 2\mathrm{H_2O}$$

In other words, carbonic oxide, in reality, is burnt at the expense of pre-existent perhydrone, not in any "direct" way, at the expense of oxygen.

In most cases of oxidation under laboratory conditions,

the agents used are salts and therefore electrolytes. The only agents which are not are perhydrone and oxygen (or ozone) itself. There is much evidence to show that these are inert in themselves; they need the aid of a determinant. Thus, to make perhydrone effective, it is commonly associated with ferrous sulphate and is probably active as the perhydrol $\mathrm{Fe}\left\langle\begin{array}{l}\mathrm{SO_3H}\\ \mathrm{O{\cdot}OH}\end{array}\right.$, an electrolyte. The oxidases, to which reference has been made, seem to be, in the main, colloid catalysts—substances which are reversibly hydroxylisable and convertible into perhydrols. Some are undoubtedly iron or manganese compounds. Apparently, the activity of these is largely dependent upon the effective acidity of the medium in which they are placed and they are mostly active only if this be near to the point of neutrality.

Control of Oxidation

Warm-blooded animals are gifted with a remarkably efficient heat-controlling mechanism. Considering the high average temperature of the blood and the amount of easily oxidisable material available, it is probable that, without such control, temperature would rapidly rise to "impossible" heights, as in fever. The question may be put: To what extent, if at all, is any chemical control exercised? It is only during recent years that special attention has been called—particularly by Moureu and Dufraisse—to the way in which an oxidation may be antagonised and potential oxidation prevented by the presence of a second oxidisable substance. The aldehyde acrolein, $CH_2{:}CH{\cdot}CHO$, a highly volatile, tear-exciting liquid, is extraordinarily sensitive to oxidation; it soon becomes acid and then rapidly passes over into a hard,

resinous condensation product. This and similar changes are prevented by a whole series of oxidisable substances —phenol, quinol, pyrogallol, even by potassium iodide, only a minute proportion of the antagonising agent being necessary.

Many such instances are known. Phosphorus does not glow in the presence of a trace of volatile oil. Solutions of ferrous sulphate and of alkaline sulphite, taken separately, are easily oxidised by air: in admixture, they are not. Perhaps the most remarkable instance is that already referred to—the prevention of the interaction of hydrogen and oxygen at a platinum surface by carbonic oxide, which itself is not oxidisable at such a surface, however.

It may well be that such antagonisms play a determining part, at least at times, in the economy of animal and plant life. Poisoning by hydrogen cyanide has long been thought to be a consequence of the inhibiting effect on oxidation which it exercises at certain nerve centres. It at once puts a stop to the evolution of oxygen from perhydrone by yeast and also by finely divided platinum. Arsenic may perhaps have a similar influence. It is conceivable that the intense poisonous activity of some alkaloids may be of a like order: it cannot be a mass effect, the quantity required is so minute. In plants, the protection of the chlorophyll mechanism against oxygen may well be secured by the presence of xanthophyll, if not of carotinene, the two compounds which are ever associated with the chlorophyll. The nearest explanation of such antagonistic actions would seem to be that the oxidisable materials in competition are "reversibly" oxidised and converted into "perhydrols," which in turn interact, reproducing oxygen and the original substances.

Such matters are assuming great technical importance in connection with the internal combustion engine, using vaporised liquid fuel. The various petrols differ greatly

in explosive behaviour—in the rapidity with which they are "burnt." The most successful regulative agent hitherto used has been lead tetrethide, $Pb(C_2H_5)_4$. It would seem likely that the effect this exercises—whatever its precise nature—must depend upon the lead functioning as an oxidising "catalyst."

Lastly, we are becoming more and more alive to the fact that life is regulated by a number of mysterious secretions from special glands, in different parts of the body —the pituitary, the thyroid, etc. Our vegetable food is proved to contain accessory factors or adjuvants, in minute amount, in absence of which nutrition breaks down.

Another case in point is Insulin, a characteristic pancreatic secretion but of frequent occurrence in animal tissues and apparently also in yeast. If used in very small amount, this material makes good the disturbance in function, whatever it may be, from which diabetics suffer; actually, it causes the disappearance of glucose from the blood. Such agents are all active in very minute amount and their effect would appear to be regulative. One of the most striking cases yet brought forward is the apparent need of a most minute, indeed altogether infinitesimal, amount of borate by the nodules which form on the roots of leguminous plants. Unless borate be present, the nodular organisms, it is asserted, are not brought into effective, reciprocal relationship with and fed by the plant.

The chapter is one of infinite importance in its vital connection but scarcely entered upon as yet, especially on the theoretical side.

The Colloid Nature of Natural Products

Apart from the compounds dissolved in the cell fluid and certain reserve materials (the simpler sugars), the

components of animal and plant structure are all highly complex, slightly soluble, if not insoluble materials—proteins for the most part. The term Colloid was early applied to them by Graham, because of their glue-like character. It is to be deplored that the term has been widened and applied generally to finely divided materials in suspension in liquid media—still more that a bastard, hybrid nomenclature has been developed which successfully serves but to obscure the obscure. As Jacques Loeb has shown, when the proteins are fairly considered from a chemical standpoint, they are as other compounds in general behaviour.

Solubility

Thus far, the phenomena of solubility have been dealt with in the vaguest possible manner; structural considerations have scarcely if at all been taken into account.

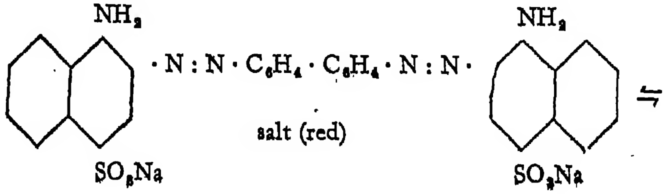
Solid paraffin is not even wetted by water: the hydrogen in it would appear to be unattractive and in the "saturated state" in which the carbon is present this also, apparently, has no residual affinity to water. Yet the molecules are not without residual affinity. Sir William Bragg's X-ray measurements show that when paraffin is fused upon glass and then cooled, the molecules become ranged like scaffold poles side by side and these interlocked poles become erect and ranged in rows. When the terminal group is oxidised and the paraffin is converted into stearic acid, it is wetted by water but only at the carboxylic tip: in other words, it is soluble at the tip but not as a whole. The higher fatty acids form such films upon water, the molecules standing upright, side by side, the carboxylic tips resting upon the liquid. The paraffins are efficient lubricants, because they are so slightly attracted to solid surfaces. All other

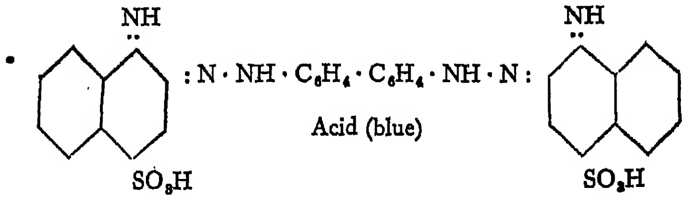
fluids are more or less "held" by the surface, their "grip" depending upon the nature of the surface and the character of the material; this is clearly a function of structure and the effect would seem to be exercised at and upon the centres of residual affinity in the molecules.

It would seem to be permissible and rational to extend this point of view to substances in solution. Difficult as it may be to define the term solubility and confine its use, it were time that we had some definite conception of the nature of the reciprocal relationship of solvent to "dissolved" substance. In view of what is said above, stearic and oleic acid may be said to be in solution only at the carboxylic tip. When the alkali-metal salts of these acids (soaps) are dissolved in water, again only the carboxylic tip is in solution: definite reciprocal relations are established between it and the near-by water molecules but the rest of the molecule is to be thought of as merely making a hole in the water, as it were. Hence, perhaps, we may arrive at a distinction between dissolved and undissolved substance and picture this as, in a measure, analogous to that to be drawn between airship and balloon. The balloon but makes a hole in the air. It is a mere floating body, itself mechanically inert but knocked about by the impacts of the air molecules. So is the *body* of the airship—like the balloon, it merely makes a hole in the air. In virtue of the engine and propeller, however, as the propeller grips the air, the airship is brought into more active relationship with the air; at least, it has a directing mechanism, though, as in the balloon, the interaction between ship and air is purely kinetic—no selective affinity of any kind comes into play. A neutral particle—if there be such—suspended in a fluid may be pictured as in the condition of the balloon; under the microscope, the particles are seen

to be in rapid movement (Brownian motion), due apparently to their bombardment by the active unit-molecules within the liquid. Perhaps the only strictly neutral particle conceivable is that of a paraffin—all other materials seem to be possessed of some degree of surface attraction, to display some affection for fluid molecules in general.

The airship, however, is the analogue of nearly all organic molecules more or less soluble in water. There is an all but insoluble body, often very large, which is associated with a radicle more or less avid of water. Alcohol is a derivative on the one hand of the hydrocarbon ethane C_2H_6, which is insoluble in water; on the other hand, of hydrone, being formed by the withdrawal of an atom of hydrogen from each and the fusion of the residues. It is miscible with water in all proportions—such is the avidity of the residual OH for water. None the less the ethane residue is to be thought of as but dragged under by the associated oxygen. Benzene, C_6H_6, spreads out as a layer upon water and is practically insoluble; phenol, $C_6H_5\cdot OH$, is but moderately soluble; the sulphonic acid, $C_6H_5\cdot SO_3H$, formed by the interaction of benzene and sulphuric acid, is intensely soluble. A large class of dyestuffs, the direct cotton dyestuffs, is formed from benzidine, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, an insoluble material, by coupling it through the agency of the NH_2 groups with certain more or less complex sulphonic acids. Congo-red is one of these:





Acid (blue)

The slight "solubility" of this huge molecule may be ascribed to the two primary SO_3H groups. As a matter of fact, there is reason to believe that the dissolving influence this group usually exercises is greatly lowered in amino-compounds of the type shown by the "control" exercised by the basic nitrogen atom. The lower sugars are easily soluble—cane sugar liquefies in one-third of its weight of water. As already explained, in these each carbon atom carries an oxygen atom and the oxygen atoms undoubtedly are centres of attraction for "water." As complexity grows, the sugars become less soluble and starch is practically insoluble; in some way, the residual affinity of the oxygen atoms becomes lowered. Starch, however, is a typical colloid when properly distributed in water. The proteins are equally so. In these, the centres of attraction are either oxygen or nitrogen and such centres are frequently repeated. Such colloids may be pictured as having "water" collected about them at the various active centres. They are "held up," as it were, by these, in the liquid. Only compounds of this type deserve the name of colloids.

If such be a true picture, we cannot well say where dissolution begins and where it ends; the passage from soluble to insoluble must be continuous. Degree of solubility must be a question of relative affinity as between the molecules of solute, between the molecules of solvent, and between the molecules of solvent and solute, that of the molecules of solute being more and more easily overcome the greater the attraction exercised

by the molecules of solvent. From this point of view, the plasticity of clay is practically the "plasticity" of thin films of water. Very finely divided (deflocculated) particles of clay, in an alkaline medium, may be pictured as in the condition of soap molecules swimming in water; if the medium be made acid, in either case, molecules are formed which have less affinity for water and therefore, tend to aggregate. Finely suspended matter may be of three kinds: acid, alkaline or neutral. Neutral particles show no tendency to wander to either electrode in an electrolytic field, the acid form wanders to one electrode, the alkaline to the other. In this behaviour we may have before us what may be visualised as happening to dissolved (potential) electrolytes.

NOTE, *January*, 1927.—One of Pasteur's earliest studies was that of vinegar manufacture, in which alcohol is oxidised to acetic acid with the aid of an organism, *Bacterium aceti*. It has long been supposed that the oxidation is effected entirely by atmospheric oxygen. It has recently been shown, however, that oxygen is operative only in the conversion of the alcohol into aldehyde. The acid is formed by the interaction of two molecules of aldehyde, as displayed on p. 101. Even two different aldehydes may be thus caused to interact and the one oxidised, the other reduced. It is thought that a specific catalyst is concerned in this "reciprocal hydrolysis." In the ordinary (alcoholic) fermentation process, apparently, acetic aldehyde is reduced at the expense of pyruvic aldehyde.

1909

A DREAM OF FAIR HYDRONE

(A CHEMICAL IDYLL)

Prologue

Fire-damp or dampf—the fiery vapour of coal-pits—the explosion of which has often given rise to the most terrible catastrophes, also known as marsh gas on account of its production when vegetation decays in stagnant water, is the simplest *hydride* of carbon, being represented by the formula $\mathbf{CH_4}$.

This gas is the absolute foundation stone of organic chemistry. Systematists call it *methane*, on account of its relation to the alcohol present in wood spirit, *methylic alcohol*, $CH_3(OH)$, which is formed from it by the process of *hydroxylation*, by the displacement of one of its atoms of hydrogen by the compound radicle [1] *hydroxyl*, OH—that is to say, water, HOH, less an atom of hydrogen, consequently worth just as much as the hydrogen atom as a combining unit.

Methane, in comparison with the hydrides of most non-metallic elements other than carbon, is strangely lacking

[1] The term *radicle* is applied not only to the simple atom but also to a group of atoms which is able, as a whole, to exercise the functions of an atom, by taking its place.

in positive qualities. It is gaseous at temperatures far below the ordinary zero, its boiling-point being $-164°$, not so very far from that of liquefied oxygen ($-182°$) and nitrogen ($-195°$) gases, which is clear proof that its molecules have but very little tendency to cling together.

Methane is the initial term of the paraffin series of hydrocarbons the compositions of which is represented by the general expression C_nH_{2n+2}. Paraffin, the white waxy solid, known best in the form of paraffin candles, is so named on account of its indifference (*parum affinis*) to almost all chemical agents, even ozone; the name is equally descriptive of all terms of the series from methane upwards. Solid paraffin is a mixture of higher terms of the series, the various constituents of petroleum—petrol, burning oil, the mineral lubricating oils and vaselin—consisting for the most part of intermediate terms.

Methane is remarkable among hydrides as that in which hydrogen is present in the highest atomic proportion in which it is known to occur in any simple hydride, the typical hydrides being as follows:

HCl	H_2O	H_3N	H_4C
Hydrogen chloride	Hydrogen oxide	Hydrogen nitride	Hydrogen carbide

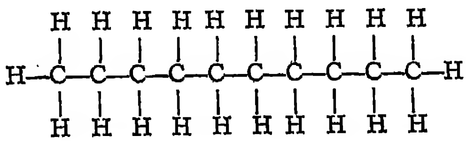
As no compound of two elements is known in which a single atom of hydrogen is associated with more than a single atom of any other element, it is to be supposed that in all these hydrides the several hydrogen atoms are separately attached to the single atom upon which they attend. The valency or atom-fixing power of hydrogen being taken as unity, that of other elements which form hydrides is indicated by the number of hydrogen atoms with which they severally unite.

If it be granted that the hydrogen atom can be united directly with but one other atom—in technical phraseology, that hydrogen is always a monadic or univalent element—it follows from the properties and composition of methane that a single atom of carbon unites with and is satisfied by four atoms of hydrogen; in other words, it is tetradic or quadrivalent. The molecule is practically saturated: that is to say, it has little if any attractive power or tendency to unite with other molecules; moreover, what is true of a single carbon atom and its associated hydrogen atoms is equally true of the more complex systems of which the higher paraffins consist.

As the hydrogen atom cannot serve as the link between other atoms, it necessarily follows that in the terms above methane the carbon atoms are linked together among themselves and that only their spare affinities are to be regarded as satisfied by hydrogen atoms.

Thus the first homologue of methane—the term next to it in the paraffin series—ethane, C_2H_6, is necessarily regarded as a compound in which two tetrad atoms of carbon are united by one affinity of each atom, leaving six affinities which are satisfied by six hydrogen atoms or $C_2H_6 = H_3C \cdot CH_3$.

The composition of the higher terms is expressed similarly on paper, *decane*, for example, by the formula:



Such hydrocarbons, it will be obvious, consist of a succession of terms each of the value CH_2 and of two end terms each of which contains an additional atom of hydrogen: hence the expression of their composition by the formula C_nH_{2n+2}.

These conclusions as to the constitution of paraffin hydrocarbons, based on the simple assumptions that hydrogen is a monadic and carbon a tetradic element, have been completely verified in practice. For example, if methylic alcohol, $CH_3(OH)$, be converted by the action of hydrogen iodide into methylic iodide and this latter be subjected to the action of a metal, the iodine is withdrawn and the hydrocarbon residue or radicle CH_3 at once unites with a second such group of atoms formed from another molecule of the iodide :

$$CH_3I - I = CH_3 ; \; CH_3 + CH_3 = H_3C \cdot CH_3$$

The process is precisely similar to that by which hydrogen gas is formed from hydrogen iodide :

$$HI - I = H ; \; H + H = H_2$$

If the iodide prepared from ethylic alcohol, $C_2H_5(OH)$, be used, diethyl or tetrane is produced :

$$CH_3 \cdot CH_2I + CH_3 \cdot CH_2I + 2\,Na = 2\,NaI + CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$$

If a mixture of two iodides be submitted to the action of the metal, the respective hydrocarbon radicles become united : thus :

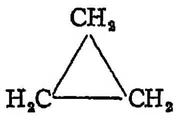
$$CH_3I + CH_3 \cdot CH_2I + 2\,Na = CH_3 \cdot CH_2 \cdot CH_3 + 2\,NaI$$

Hydrocarbons of any degree of complexity may be built up in this manner.

The operation is akin to that of forming a simple chain by forging link upon link ; on this account, such conjunctions of simple hydrocarbon radicles are spoken of as open-chain hydrocarbons. Apparently there is no limit to the length of such *open chains*.

But *closed chains or rings* of carbon atoms may be formed by linking the ends of open simple chains together. For example, if trimethylene bromide, $BrCH_2{\cdot}CH_2{\cdot}CH_2Br$ (which is to be regarded as propane, $CH_3.CH_2.CH_3$, in which an atom of hydrogen in each of the CH_3 groups is displaced by an atom of bromine) be subjected to the action of sodium, it is not only deprived of the two bromine atoms but the two ends of the chain become linked together :

$$BrCH_2 \cdot CH_2 \cdot CH_2Br - 2Br =$$



Even two carbon atoms may be united in a closed ring, as in ethane or ethylene, which is formed by mixing alcohol with concentrated sulphuric acid and heating the mixture :

$$\begin{array}{l} CH_2 \cdot OH \\ | \\ CH_2H \end{array} = \begin{array}{c} CH_2 \\ () \\ CH_2 \end{array} + OH_2$$

Apparently it is not possible to convert every open-chain hydrocarbon into the corresponding ring system—the most complex compounds of this kind known at present contain only seven atoms of carbon.

The recognition of such limitations necessitates the recognition of structural peculiarities in the carbon atoms, the effect of which is to limit their activity, so that they can only be arranged in a certain limited number of ways. It is important that these peculiarities should be noticed. (See ante, pp. 74, and 137.)

A model or symbol in remarkable accord with the general chemical behaviour of carbon is afforded by the regular tetrahedron. Assuming such a tetrahedron to be

inscribed inside a sphere, the centre of influence of the carbon atom may be supposed to be at the centre of the sphere and the four affinities of the atom may be thought of as directed outwards towards the four solid angles of the tetrahedron ; in this arrangement, the angle included between two affinities is 109°28′.

Such a model is easily constructed by joining together at their edges four equilateral triangles cut out of cardboard. For the purpose of studying the manner in which carbon atoms can be united together, it is better to bend two pieces of wire at an angle of 109°28′ and then to solder these together at the bend in such a way that the plane passing through the two arms of the one is at right angles to that passing through the two arms of the other. The four arms should be made of equal length. Such model carbon atoms can be united by juxtaposing an arm of each of two skeleton tetrahedra and then binding these together. Provided they be arranged in spiral order any desired number may be united in such a manner but the number which can be arranged so that their centres lie in one plane is strictly limited : five naturally form a ring which is practically complete ; *any less number gives an incomplete ring* : the significance of this peculiarity will be discussed later on. Models of the higher paraffins made with such skeleton tetrahedra present the appearance of curls rather than of straight chains.

The adoption of this tetrahedral conception of the functional activity of a carbon atom is justified in the most absolute manner possible by the discovery which is so indelibly associated with the name and fame of the great Pasteur—namely, the discovery of two modifications of tartaric acid identical in composition, which are distinguishable only by a minute difference in crystalline form and by their behaviour in polarised light : a solution

of the one having the power of deflecting a beam of polarised light just as far to the right as an equally concentrated solution of the other will to the left. In tartaric acid

$$\begin{array}{l} \mathbf{C}H\,(OH)\,(COOH) \\ \mathbf{C}H\,(OH)\,(COOH) \end{array}$$

each of two carbon atoms—those printed in clarendon type—is associated with four different radicles H, (OH), (COOH) and [CH(OH)(COOH)].

If two large cardboard tetrahedra be taken, the one without one of its sides so that it can be superposed upon the other, it is easy to fix four differently coloured caps over the four solid angles of each tetrahedron so that when the two tetrahedra are superposed like colours occupy like positions on each. Now take off the capping tetrahedron and place the other in front of a mirror or looking-glass: note the position of the coloured angles on the image and assume that the tetrahedron used as cap is in the position of the image, then arrange the colours at its angles so that they are in the position which they occupy in the image; superpose this capping tetrahedron on the other: the two no longer fit, in the sense that the coloured angles match. In fact, two non-superposable models are obtained but it is only when all four angles are differently occupied that two non-superposable forms are possible.

Applying this argument to the atom itself, the conclusion is arrived at that a compound such as tartaric acid in which the four affinities of a single carbon atom are satisfied by four different units or radicles may exist in two forms: the fact that these are optically active to equal extents but in different directions being accounted for by the spiral arrangements in space in reverse order of the four radicles in the two compounds.

A carbon atom in the condition pictured is termed an *asymmetric* atom, as such a system as that described has no plane of symmetry—in other words, it cannot be cut into halves. Asymmetric carbon plays a dominant part in Nature; it may, indeed, be said that it is the Rosetta stone with the aid of which it is becoming possible to arrive at an interpretation of the fundamental phenomena of life in so far as these can in any way be made clear by the chemist.

Argument

The hydrides of chlorine, oxygen and nitrogen—hydrogen chloride, hydrogen oxide and hydrogen nitride (ammonia)—are compounds the behaviour of which is in striking contrast with that of the simplest hydride of carbon. Three of these four hydrides are gaseous far below ordinary temperatures:

	HCl	H_2O	H_3N	H_4C
Mol. wt.	36·4	18	17	16
B.P.	-83°	100°	$-38{\cdot}5^\circ$	-164°

hydrogen oxide alone liquefying without compulsion. The degree of readiness with which they pass into the liquid state obviously, however, bears no relation to their molecular weights, which differ but slightly in three cases, the fourth compound (hydrogen chloride) being intermediate in volatility between the two which are less than half as dense.

The mere fact that hydrogen oxide becomes water so readily must be held to be proof in itself that the molecules of the oxide are gifted in a high degree with attractive forces which lead them to combine *inter se*. No such evidence of mutual affinity is met with either in the case of hydrogen chloride or in that of ammonia but although these have no tendency to fall victims to self-love their

affection for water is extraordinary, the former being soluble to the extent of nearly 500 volumes and the latter to the extent of about 1,100 volumes in one volume of cold water. A solution of hydrogen chloride saturated at 0° contains about 82 parts of the chloride to 100 of water, corresponding to the ratio $HCl : 2{\cdot}4OH_2$. A solution of ammonia saturated at 0° contains about 87 parts of the nitride per 100 of water, corresponding to the ratio $NH_3 : 1{\cdot}1OH_2$. Hydrogen oxide also, it may be pointed out, is undoubtedly soluble in water at all temperatures but it is impossible to measure its solubility.

Still more striking proof of the unsaturated nature of hydrogen chloride and nitride is afforded by the manner in which these two gases at once interact when brought into contact, forming solid ammonium chloride, NH_4Cl, a well-defined crystalline substance.

Whilst, therefore, a single atom of carbon combines with four atoms of hydrogen and these four atoms of hydrogen satisfy it and are satisfied by it practically entirely, no one of the other three elements considered is satisfied by the number of hydrogen atoms with which it can combine—in other words, chlorine, oxygen and nitrogen in contradistinction to carbon are all possessed of a greater atom-fixing power, a higher valency, than is indicated by their affinity for hydrogen.

This higher or extra valency is a function of a different order from the normal or hydride valency, as it may be termed: the latter being a fixed, the former a variable and dependent function.

Thus if the hydrogen in hydrogen chloride be displaced by the hydrocarbon radicle methyl, CH_3, a neutral and practically inert substance, methyl chloride, CH_3Cl, is produced. In like manner both methyl alcohol and methyl ether, $CH_3{\cdot}OH$ and $CH_3{\cdot}O{\cdot}CH_3$, are not only far less active substances than water is but their boiling

points are considerably lower than that of water, the alcohol boiling at 66°, the ether being a gas although of higher molecular weight than the alcohol. If methyl be substituted for hydrogen in ammonia, it has little influence on the nitrogen in depriving it of its power of attracting acids; the solubility in water of the amine $(CH_3)_3N$, however, is much lower than that of ammonia, whilst the boiling point is much higher. In the case of aniline, $C_6H_5 \cdot H_2N$, which is derived from ammonia and from phene or benzene, C_6H_6, containing as it does the radicle phenyl, C_6H_5, in place of one of the atoms of hydrogen of ammonia, the basic tendencies of the nitrogen atom are almost neutralised, aniline being a very weak base in comparison with ammonia. If the phenyl in aniline be modified or weighted by introducing chlorine atoms in place of several of its hydrogen atoms, the basic properties are still further weakened and eventually entirely neutralised, trichloraniline, $C_6H_2Cl_3 \cdot H_2N$, having no power of combining with acids.

It is not easy, scarcely possible, indeed, to embody facts such as these in models corresponding to that by which carbon is represented, which gives expression so faithfully to its dominant qualities.

In the case of carbon, a tetrahedron with four rods directed from its centre and fixed rigidly at its four terminal points serves to indicate both the number of affinities at the disposal of the carbon atom and the direction in which, apparently, these can act. Hydrogen, like carbon, being also an element of steadfast behaviour, its valency never exceeding unity, may be represented similarly by a ball provided with a single hole into which the rods representing the single combining affinity may be rigidly inserted. Such models serve to emphasise the fact that hydrogen and carbon respectively act invariably as monadic and tetradic elements.

These are circumstances which it is of importance to emphasise, for if it be the fact that hydrogen is a consistent monad, it necessarily follows that the residual affinity which is manifest in so high a degree in hydrogen chloride, oxide and nitride is in no way resident in the hydrogen but entirely in its associate—that is to say, in chlorine or oxygen or nitrogen; the residual affinity of these elements is of such nature, moreover, that it cannot be satisfied either by hydrogen alone or by any equivalent radicle such as methyl.

To express the peculiar behaviour of oxygen, a ball may be taken through which pass two rods, both free to move in and out. When both rods are drawn out to the maximum extent, the model represents dyad oxygen as it is in a saturated compound; when, however, the rods project partly on both sides of the sphere, the model is indicative of the tetradic condition of oxygen, the intensity of the secondary or extra valency being indicated by the extent to which the rods project. For example:

This method of representation is not applicable, however, to chlorine and nitrogen, as these elements both increase in valency to the same extent as oxygen does, that is to say, to the extent of two units, two latent affinities becoming active in both cases when the normal or hydride valency is exceeded. At present we have no explanation to offer of these peculiarities. The formulae of the several hydrides considered are best written, therefore, simply as follows:

$$HCl< \qquad H_2O< \qquad H_3N< \qquad H_4C$$

to indicate the existence of unsaturated affinities and their number in the dominant element in three of the four compounds.

It will be desirable now to consider the nature of the compounds formed by the association of the hydrides of chlorine, oxygen and nitrogen. That formed from hydrogen chloride and ammonia may be taken first, as it is a well-defined stable compound derived from single molecules of the two substances:

$$NH_3 + HCl = NH_4Cl$$

The composition of this compound, *ammonium chloride*, has been the subject of much discussion in days gone by. In the first place, it is noteworthy that it resembles most closely in all essential particulars the haloids or metallic halides such as common salt, NaCl, potassium chloride and similar substances—the compound radicle ammonium NH_4, playing a part in it exactly similar to that of the simple metallic radicle in these latter. From this it may be argued that, when interaction takes place, the hydrogen and chlorine in hydrogen chloride part company and combine separately with the nitrogen of ammonia. If this were not the case and the hydrogen atom of the chloride retained its individuality in the new compound it should be possible to obtain different derivatives according as this hydrogen atom or one of those in ammonia were displaced by some equivalent radicle such as methyl. Calling the three hydrogen atoms in ammonia *a b c* and that in hydrogen chloride *d*, if the four atoms of hydrogen *a b c d* in ammonium chloride be of equal value, it should not matter in what order they are displaced. If, however, *d* be different from *a b c* and different radicles were introduced in place of the four hydrogen atoms at one time in one order and at another

time in another, the result would be different. A large number of such substituted ammonium compounds have been prepared but in no case has any such difference been met with. It is therefore assumed that in ammonium chloride the four hydrogen atoms are of equal value and symmetrically distributed about the nitrogen atom and the associated negative radicle.

In the case of ammonia itself, the functional identity of the three hydrogen atoms has been established beyond question by preparing from it substituted ammonias by introducing three different radicles *a b c* in place of its three hydrogen atoms. Whatever the order in which the radicles are introduced, whether it be

a b c *a c b* *b a c* *b c a* *c a b* *c b a*,

the product eventually obtained is always one and the same substance.

This conclusion—that, when hydrogen chloride and ammonia interact, a rearrangement takes place, as the result of the separation and independent association of the elements of the hydrogen chloride molecule with the nitrogen atom of the ammonia molecule—has far-reaching consequences if the argument be extended to the other elements under consideration.

Then it may be asked, What happens when ammonia is brought into contact with water? It is clear that the two compounds interact in some way. Is the behaviour of hydrogen oxide towards ammonia in any way similar to that of hydrogen chloride? It may be supposed that, like this latter, it is divisible into two radicles, H and OH. Is it so divided and do these radicles enter separately into combination with the nitrogen atom, forming ammonium hydroxide, $NH_4{\cdot}OH$? Since ammonium chloride is the analogue of sodium chloride,

ammonium hydroxide should be very similar to sodium hydroxide or caustic soda, Na(OH). In point of fact it is so only to a very slight extent. The conclusion is forced upon us, therefore, that a small but only a very small proportion of ammonium hydroxide is formed when ammonia dissolves in water. As dissolution takes place so readily and to such an extent, it is difficult to avoid the conclusion that combination does take place and it seems not improbable that a compound such as is represented by the formula $H_3N = OH_2$ is the main product. Apparently, therefore, ammonia has much less influence over hydrogen oxide than it has over hydrogen chloride.

Applying a similar argument to hydrogen chloride dissolved in water, it may be supposed that chloride and oxide interact in the following manner :

$$H_2O + HCl = H_2O\langle{}^{H}_{Cl}$$

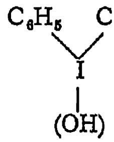
This product, being unstable and having no tendency to crystallise under ordinary conditions, cannot be isolated. But sulphur—which is own brother, as it were, to oxygen among the elements—gives rise to compounds of this type, such as trimethylsulphonium chloride, $S(CH_3)_3Cl$. There is, therefore, every reason to believe that compounds of oxygen may exist such as that postulated above.

The question arises whether the reciprocal interchange be not also effected, namely :

$$HCl + H_2O = HCl\langle{}^{H}_{OH}$$

For reasons which cannot well be discussed in this article, it is more than probable that it is. This conclusion also finds support in the argument from analogy. Thus

iodine, which is so closely related to chlorine, is known to give rise to well-defined compounds in which it exercises the functions of a triad, such as—



(Diphenyliodonium hydroxide)

which, it may be pointed out, is an altogether remarkable compound, inasmuch as it has the properties of a caustic alkali, the group $(C_6H_5)_2I$ exercising the functions of the atom of sodium in sodium hydroxide. Such are the wonders of chemistry!

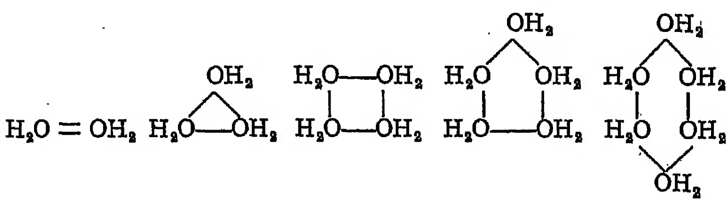
To carry the argument one stage farther: the compound $(CH_3)_3SCl$, in which sulphur functions as a tetrad, contains only two different radicles. If, in place of the three similar hydrocarbon radicles, three which are different be associated with a sulphur atom, optically active compounds are produced, as in the case of carbon. In this way proof is obtained that sulphur can simulate carbon: the tetrahedron becomes the model of the sulphur atom as well as of the carbon atom. Since oxygen is very closely related to sulphur, it may be assumed that oxygen also can exercise "tetrahedral" functions and that it may be expected to behave more or less like carbon. In not a few cases it does. Thus a number of compounds is known in which four atoms of carbon are associated with one atom of oxygen in a ring. Such rings are formed with exceptional readiness, so that it would seem to be probable that the directions in which the affinities of the oxygen atom act naturally are not very different from those in which the affinities of carbon act. Such arguments must not be pressed too far; the depth of our inability to account for the peculiar loves and affinities of the atoms must not be forgotten.

Epilogue

We may now ask, How is liquid water itself formed from hydrogen oxide ? What may we suppose the composition and constitution of liquid water to be ? Its properties are altogether incompatible with the assumption that it consists only of simple molecules such as are represented by the formula H_2O ; yet, as steam consists of these, such simple molecules must be present in it, as the maintenace of equilibrium between a liquid and its vapour necessarily involves the constant passage of gaseous molecules from and into the liquid.

To mark the distinction between liquid water and the fundamental molecule represented by the formula OH_2 from which it is formed, it is desirable to confine the term "water" to the liquid and to term the fundamental molecule *Hydrone*.*

Hydrone is comparable with the hydrocarbon radicle methylene, CH_2, which, however, cannot exist *per se*, its affinity for itself being of such intensity that when freed from other radicles it at once polymerises, giving rise to dimethylene or ethene (ethylene), $H_2C{=}CH_2$. It is to be supposed that hydrone behaves in a similar manner : that is to say, that when it becomes liquid water it gives rise to a series of polyhydrones corresponding to the polymethylenes, thus :



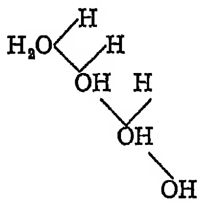
Dihydrone Trihydrone Tetrhydrone Penthydrone Hexhydrone

*Compare *Royal Society Proceedings*, 1908, A, vol. 81, 80.

In addition, interaction probably takes place in the manner pictured by the expression

$$H_2O + H \cdot OH = H_2O{<}^{H}_{OH} \quad \text{(Hydronol)}$$

And it is both conceivable and indeed probable that still longer hydronol chains are also formed, such as



In short, the picture to be formed of the state of water is that of a complex mixture of molecules of the general composition $(OH_2)_x$, x having many values, the proportion in which various kinds of molecules are present being determined by the external conditions (temperature and pressure). Although quiet in appearance, the internal condition of the liquid must be supposed to be one of unceasing turmoil, owing to the perpetual passage backwards and forwards of the various molecules from one state of complexity into another, as summarised in the expression

$$(H_2O)_x \rightleftarrows xOH_2$$

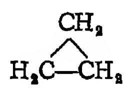
As to the activities of the various molecules, there must be great differences between them. The hydrone molecules are undoubtedly the most active; and next to these come the molecules of hydronol: the increase in the activity of water as its temperature is raised may, in fact, be ascribed to an increase in the proportion of

hydrone and hydronol in the liquid. As to the activity of the polyhydrones, it is possible to form an opinion only on grounds of analogy.

In the case of the polymethylenes, the activity diminishes from ethylene to pentamethylene. Thus ethylene combines with the greatest readiness with bromine and with hydrogen bromide:

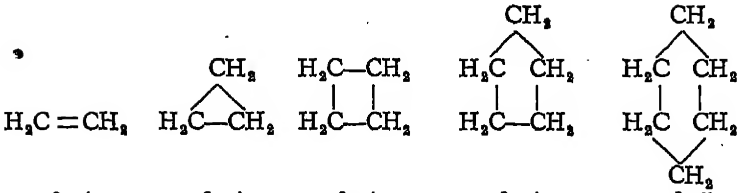
$$H_2C{=}CH_2+Br_2=BrCH_2{\cdot}CH_2Br \qquad CH_2{=}CH_2+HBr=CH_3{\cdot}CH_2Br$$

The higher polymethylene rings remain unbroken when submitted to the action of bromine but the trimethylene ring is without difficulty opened out by means of hydrogen bromide:


$$+\,HBr = CH_3 \cdot CH_2 \cdot CH_2Br$$

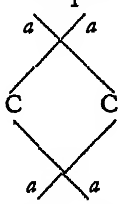
The tetramethylene ring is somewhat less readily ruptured and the penta- and hexa-methylene rings are unaffected by hydrogen bromide. (See Introduction.)

Assuming that the configuration of the carbon atom is tetrahedral and that the affinities act in the manner pointed out above, the angle at which two affinities meet is 109°28′. To account for the behaviour of the different polymethylenes, von Baeyer has argued that if it be supposed that in the formation of ethylene two affinities of the one carbon atom become united with two affinities of the other carbon atom, the affinities would be forced from their normal angular positions into parallelism—that is to say, through an angle of $\frac{109°28'}{2} = 54°44'$—but in the case of the higher polymethylenes the distortion would be less, thus:



54°44′ 24°44′ 9°34′ 0°44′ −5°16′

The general behaviour of the hydrocarbons under consideration, however, is scarcely that of stressed molecules but rather that of molecules endowed with various degrees of attractive power. If von Baeyer's argument be so modified that it be supposed that the affinities, instead of being deflected, act practically at their proper angle and more nearly neutralise one another the more nearly they come into parallelism, the angle *a* at which the affinities meet may be taken as a measure of the free affinity latent in the molecule; and the larger the angle the greater will be the activity of the compound. Ethylene (dimethylene) from this point of view



is an eminently unsaturated compound; whilst pentamethylene is all but saturated, as the several pairs of affinities nearly overlap,* the angle *a* being reduced almost to nothing.

* This argument will be best understood if a graphic construction be resorted to. For this purpose a number of V-shaped strips, cut to an angle of 109° 28′, should be made out of cardboard. These are conveniently made three-quarters of an inch wide and the two limbs may be each 6 inches long. Lines should be ruled down the middle of each limb; the cardboard should be perforated 3 inches distant from the point of intersection of the two lines on each strip. By joining such strips together at the perforated points in twos, threes, fours, fives and sixes by means of drawing pins placed head down on the table and then fixing the joint by covering the points of the pins with discs of cork, models are obtained which represent the various systems.

Assuming, for the reasons already stated, that the tendency of oxygen is to simulate carbon, it should follow that the activity of the polyhydrone molecules in water diminishes progressively as they increase in complexity: consequently that penthydrone is practically inactive.

If water consist on the one hand of simple molecules which have a strong tendency to cling together and on the other of relatively heavy inert molecules, such as those of penthydrone $(OH_2)_5$, it is easy to understand why it boils at such an elevated temperature as 100°.

A point is now reached at which the story becomes exciting; it is therefore time to write, "To be continued in our next."

In conclusion it may be asked, Can water be the subject of an idyll? An idyll has been defined as a poem which has for its object a vivid and simple representation of ordinary objects in pastoral nature or of scenes or events of pastoral life. Tennyson, however, has written the *Idylls of the King*. Kings are scarcely common objects of the seashore, whilst water certainly is prominent among these and a true king among earthly materials: therefore it may well form the subject of an idyll and this story may be added to the many other marvellous tales that are told of its mysterious ways and wondrous doings.

Being thus brought into Wonderland, we may well recall the classical assertion of the Duchess, "'Tis love, 'tis love, that makes the world go round." Had she lived in these days, having studied physiography at school and college, she would have been aware perhaps that water is the primary moving spirit on our globe; that even love is not possible without water—indeed, that the part which water plays in conditioning life and in the maintenance of life is such that its importance cannot be exaggerated.

Yet it is daily and hourly used and wasted entirely without thought!

The poetry of moisture must some day take its place along with that of motion—when all see that the earth gives forth her fruits in due season and in due measure only when fair hydrone, descending from the air above, clasps her in warm and beneficent embrace.

NOTE.—In the light of later knowledge, some of the conclusions advanced in this essay need reconsideration—particularly those relating to the polymethylenes. Using the tetrahedral model of carbon, it is impossible to form "closed systems" containing less than six carbon atoms. A complete revision of the chemistry of the group, including the terpenes, seems to be imperative. The argument may be extended to water—we have to be cautious in considering the forms that are possible. It may be added, that the chemist cannot well do otherwise, at present, than proceed upon the assumption that the atoms in molecules are closely packed.

After close study of the problem here opened up, during the passage of this sheet through the press, I am led to conclude, that whilst the models can be packed in closed systems only iu sixes, if the method described for benzene (p. 74) be adopted, a second mode of packing is possible which is applicable to the polymethylenes and numerous other compounds. The mode of union symbolized is a peculiar one. Hitherto unforeseen, the logical outcome, however, of the strict geometric use of the solid model.

1909

THE THIRST OF SALTED WATER

"A beautiful theory spoilt by a nasty, ugly little fact."
—HUXLEY.*

"It is as risky for a chemist to apply mathematics as for a mathematician to lecture to chemists: we should work in co-operation. . . . All this hangs together but it lends no support at all to the dynamically impossible theory that the ions are free."
FITZGERALD, Helmholtz Memorial Lecture.

THE impassioned eloquence and unrivalled power of appreciating natural beauty characteristic of the author of *Modern Painters* are nowhere more apparent than in the opening lines of the section "Of Truth of Water," in that work:

Of all organic substances, acting in their own proper nature and without assistance or combination, water is the most wonderful. If we think of it as the source of all the changefulness and beauty which we have seen in clouds; then as the instrument by which the earth we have contemplated was modelled into symmetry and its crags chiselled into grace; then as in the form of snow it robes the mountains it has made with that transcendent

* Vide *Memories of my Life* (Francis Galton).

light which we could not have conceived if we had not seen; then as it exists in the foam of the torrent—in the iris which spans it, in the morning mist which rises from it, in the deep crystalline pools which mirror its hanging shore, in the broad lake and glancing river; finally, in that which is to all human minds the best emblem of unwearied, unconquerable power—the wild, various, fantastic, tameless unity of the sea: what shall we compare to this mighty, this universal element, for glory and for beauty or how shall we follow its eternal changefulness of feeling? It is like trying to paint a soul.

If the painter who is called upon to deal with its surface appearance alone cannot picture water, how shall the chemist succeed in penetrating the hidden mysteries of its being? And yet, as it is his mission to display the soul in all things, the attempt must be made: a careful study of Ruskin's idealism may be of more service in instructing us how to proceed than any text-book: the counsel he gives may well be considered:

There is hardly a roadside pond or pool which has not as much landscape in it as above it. It is not the brown, muddy, dull thing we suppose it to be; it has a heart like ourselves and in the bottom of that there are the boughs of the tall trees and the blades of the shaking grass and all manner of hues of variable, pleasant light out of the sky; nay, the ugly gutter that stagnates over the drain bars, in the heart of the foul city, is not altogether base; down in that, if you will look deep enough, you may see the dark, serious blue of far-off sky and the passing of pure clouds. It is at your will that you see in that despised stream either the refuse of the street or the image of the sky—so it is with almost all other things that we unkindly despise. Now this far-seeing is just the difference between the great and the vulgar painter;

the common man *knows* the roadside pool is muddy and draws its mud; the great painter sees beneath and behind the brown surface what will take him a day's work to follow but he follows it, cost what it will. And if painters would only go out to the nearest common and take the nearest dirty pool among the furze and draw that thoroughly, not considering that it is water that they are drawing and that water must be done in a certain way but drawing determinedly what they *see*, that is to say, all the trees and their shaking leaves and all the hazy passages of disturbing sunshine; and the bottom seen in the clearer little bits at the edge and the stones of it and all the sky and the clouds far down in the middle, drawn as completely and more delicately they must be than the real clouds above, they would come home with such a notion of water-painting as might save me and every one else all trouble of writing more about the matter; but now they do nothing of the kind but take the ugly, round, yellow surface for granted or else improve it and, instead of giving that refined, complex, delicate but saddened and gloomy reflection in the polluted water, they clear it up with coarse flashes of yellow and green and blue and spoil their own eyes and hurt ours and the uninterrupted streams and maligned sea hiss shame upon us from all their rocky beds and hollow shores.

Have not we chemists done little more thus far than spoil our own eyes and shut those of others for all appreciation of water—have we not made it of little account by representing it by the thin and unattractive symbol H_2O—still more by *speaking* of it with heartless vulgarity in these later degenerate days as *Aitch-too-oh*? Surely "the uninterrupted streams and the maligned sea hiss shame" upon our science, deriding our puny efforts to explain the maddening thirst begotten in water by the salts which the unconquerable and untiring scavenger,

throughout the ages, has washed from the surface of our globe. While a Coleridge sings:

> Water, water, everywhere,
> Nor any drop to drink,

the fish, naked but unashamed, in very scorn of our weakness, swim calmly in the ocean and are not harmed. It is only too true that familiarity breeds contempt: we have so lost ourselves in muddy pools, like the common painter we have so fixed our attention on the mud, that we know nought of clean water—clear, persistent thinking alone can give us knowledge and that has been set aside of late.

Since 1885, my voice has been that of one crying in the wilderness when, time after time, I have insisted that it is essential to take the water in aqueous solutions into account—that water is altogether peculiar among solvents; the meagre answer of those who now are compelled to admit that it is active has been, "It has high specific inductive capacity"—truly a stone for bread. Apparently, the situation has been so trying to the nerves of those afflicted with ionomania that, like the burglarious railway porter in Mr. Barrie's recent play, they have elected to take the solute neat: it might be supposed because the advocates of the doctrine came from colder or damper climes than our own, where water is at a discount, were it not that, while thinking of the cordial, with strange inconsistency they have elected to deal only with beverages containing the merest dash of spirit.

But, as did Sister Anne in the fairy story, I see signs of approaching help: there is reason to think that Wotan's spear is broken at last; that the *Götterdammerung* must soon be enacted. Thus two writers in a recent number of Liebig's *Annalen der Chemie*, Messrs. Decker and von

Fellenberg, not only put forward the "original" conclusion that oxygen is to be treated as a tetradic element but, such is the encouragement given by recent revolt against imperial autocracy—actually dare to murmur against ionic supremacy. Their words are noteworthy:

In den verdünnten Lösungen von Salzsäure in Wasser ist Oxoniumchlorid anzunehmen, genau wie in den Lösungen von Salzsäure in flüssigem Ammoniak Salmiak angenommen wird und *entgegen den Auffassungen der Ionentheorie* [my italics]. Solange die letztere die Frage nach der chemischen Rolle des Lösungmittels stillschweigend umgeht, müssen ihre Ansprüche chemische Thatsachen zu erklären als ungerechtfertigt angesehen werden. Die Anzahl der offenbar zusammenhängenden Thatsachen aber, die die Ionentheorie mit Hülfe der von Faraday als glänzendes Mittel zur Veranschaulichung der Vorgänge bei der Elektrolyse geschaffenen Vorstellung der Ionen zusammenzufassen sucht, wird, wie es scheint, in der wechselnden Valenz bestimmter Atome des Lösungsmittels ihre Erklärung finden. Hierin liegt auch die grosse Bedeutung der Lehre von der Tetravalenz des Sauerstoffs. Sie ist berufen, die structurtheoretische Unterlage für die von Mendelejeff inaugurirte Hydrattheorie der wässerigen Lösungen und für das damit zusammenhängende Problem der Structur des flüssigen Wassers zu liefern.

All this of course without reference to the fact that they are recapitulating ancient history. What matters it, however, who spreads the complaint? The virus is abroad at last.

At all events the opsonic index of workers is now risen sufficiently high, it seems, to warrant the introduction of a strong dose of antitoxin. Thus another writer, who dates from Charlottenburg—that name of strange import in London—I. Traube, who also apparently is fallen a

victim to *Wassersucht*, with strange effrontery actually concludes an essay (*Berichte der deutschen chemischen Gelleschaft*, 1909, p. 94) with the impious words, "Die Theorie von Arrhenius scheint mir auf einen fundamentalen Irrthume zu beruhen." When, in very early days, I ventured to say that the speculation was an offence against chemical common sense, I was looked at askance as an infidel. For some time past, Prof. Harry C. Jones, of Baltimore, who has long been a notable trumpeter of ionic formularies in the United States, has been gradually executing strategic movements which give clear indication of a desire to beat a retreat from an impossible position. He is even beginning to claim to have been the inventor of the weapons in the hands of the opposition party—always an interesting sign of recantation. The beautiful simplicity of this writer's belief is well shown in the following passage from the preface to his *Elements of Organic Chemistry* (1903):

> Take the theory of electrolytic dissociation, which to-day is as well established as many of our laws of nature [this is not saying much for the certainty of her laws, perhaps]: it has shown us that it is the ions and not the atoms which are the active agents chemically. If the student is taught the contrary in the early stages of his work, later this must all be unlearned and we know how difficult it is to correct first impressions. . . . Further, since we know that the ion and not the atom or the molecule is the factor which enters into most chemical reactions, we should insist upon it because it is true.

The situation is painted in an equally philosophical manner in the preface to his larger work on the *Principles of Inorganic Chemistry*. It is rendered almost amusing by a statement such as the following:

The writer has refrained from introducing unproved theories and disputed questions as far as possible, since the student for whom this work is meant is scarcely at a stage to properly appreciate and evaluate scientific discussion. The attempt has, however, been made to avoid dogmatism, since this is harmful even in an elementary work.

O wad some Pow'r the giftie gie us
To see oursels as ithers see us.

Still this may be said of most of us.

Prof. Jones may have reason during the next few years to appreciate the force of his own remark, " we know how difficult it is to correct first impressions "—in any case, the example may serve to show how necessary it is to have regard for facts and to avoid creating visionary impressions.

In our own country, the physico-chemical dovecot has evidently been somewhat disturbed of late: seemingly its inmates are beginning to study the gentle art of hedging; unfortunately most of them lack the courage to release their hold of the Ostwaldian petticoats, to which they have so long been accustomed to cling that they are unable to stand alone. As was said of the lambs of little Bo-Peep—if let alone for a while longer, doubtless they will come home and leave their tales (of ions as well as of repentance) discreetly behind them.

It is time that some serious protest were made against the pedantic narrowness and dogmatism of the modern elementary text-book. If text-books were mere novels—they resemble them most closely in the entire absence of novelty of theme—it would matter little what is written in them; unfortunately the poor devil of a student is forced by a merciless examination system to commit their contents to memory and touching pitch he cannot avoid

defilement. The retirement of the censor of stage plays would probably be welcomed by playwrights; if he were charged instead with the suppression of indecent scientific literature—indecent through lack of logic and lack of most things worth knowing—he might render a real service to society.

After all, we scientific workers (or should it not rather be said we workers in science? because, although evil communications corrupt good manners, the work of science has not, as a necessary consequence, the establishment in the worker of a scientific habit of mind), like women, are the victims of fashion: at one time we wear dissociated ions, at another electrons; and we are always loath to don rational clothing; some fixed belief we must have manufactured for us: we are high or low church, of this or that degree of nonconformity, according to the school in which we are brought up—but the agnostic is always rare among us and of late years the critic has been taboo. The poor student is usually the sorely afflicted victim of our whims. Instead of setting him to read sound literature, such as the *Life of Faraday* by Bence Jones and even Faraday's researches, so that he might appreciate the spirit in which work has been done in the past, we administer the latest tips in mild doses: the poor creature's mental digestion is horribly upset and his morals remain lax—but what matters it? he can use stilted paraphrase in place of the studied simplicity of older times and is up to date, although perhaps he has no knowledge of fundamentals. Our modern methods of teaching are pretentious and too often fraudulent. We need to realise this and to change our ways.

When alcohol is mixed with water what really happens? When sugar or salt is dissolved, what is the effect produced? In all cases, whatever be dissolved in it, the

properties of the solvent water are profoundly modified—its freezing point being lowered but its boiling point raised, although in different degrees, when the substances are used in proportions corresponding to their formulae, C_2H_6O, $C_{21}H_{22}O_{11}$, NaCl, the effect produced in weak solutions by the salt being about 1·75 times as great as that produced by either alcohol or sugar. The solution of salt, moreover, differs from the solutions of the two other substances in that it is an electrolyte—capable, that is to say, of conducting an electric current.

As long ago as 1851, it was argued by Williamson, in his classical essay on the *Theory of Etherification*, that—

The formation of ether from alcohol and sulphuric acid is neither a process of simple separation nor one of mere synthesis but it consists in the substitution of one molecule for another and is effected by double decomposition between two compounds. This view of the matter (he said) is therefore consistent with the contact theory, inasmuch as it acknowledges the circumstance of contact as a necessary condition of the reaction of the molecules upon one another. . . . It may naturally be asked, how do hydrogen and carburetted hydrogen thus continually change places ? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now, in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged ; that if hydrogen and amyl can replace one another in a compound, hydrogen and ethyl, which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound ; and that the facility for interchange of hydrogen and methyl, which are still more similar, will be greater still. But if this be true, must not the

exchange of one molecule for another of *identical* properties be the most easily effected of all? Surely it must, if there be any difference at all and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among substances resembling it in other respects. We are thus forced to admit that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united but, on the contrary, is constantly changing places with other atoms of hydrogen or, what is the same thing, changing chlorine.

It is clear that Williamson thought of the decomposition as taking place during the times when the molecules were in contact. A few years later, in 1857, however, in order to account for the fact that the smallest currents gave rise to a sensible amount of electrolytic decomposition, Clausius introduced the conception of ionic dissociation—of the separation of the compound in solution into its two ions—which he regarded as conditioned by occasional violent kinetic collisions between the molecules. But his point of view was that from which the classical baby in Marryat's novel was apologised for—as being only a little one. It was not until 1883 that Arrhenius came forward as a Whole-Hogger and assumed that the dissociation might be complete or nearly so, in order to account for the increase in the molecular conductivity on diluting the solution of a dissolved salt. His conception did not become known until late in 1885, and even then did not "catch on." The way had to be prepared and

salted, as chemists were still possessed of some sanity of judgment.

In 1885, van't Hoff, assuming the character of the Hatter, invited us to a scientific Mad Tea Party, at which he out-hatted the Hatter by gravely assuring us that "I see what I eat" *was* the same thing as "I eat what I see": introducing us into topsy-turvydom, he insisted that a liquid was to be treated not as a liquid but as a gas; that the attractive forces in play between the molecules of solute and solvent were not really attractions: the solute was to be thought of as banging about and hitting things, as though it were gasified. Even this did not mislead us, mainly because, although, in the case of cane sugar, Pfeffer's pressure values—when looked at upside-down—were in accordance with the gas pressure hypothesis, salt again behaved in an irrational way, producing nearly double the effect of sugar.

Here Arrhenius got his chance and being a good sportsman he soon took it, coming forward with the suggestion that the number of molecules in the solution of salt was nearly twice as great as had been supposed, owing to the dissociation of the salt into its ions. The combination of van't Hoff's great reputation as the author of the asymmetric carbon hypothesis with Arrhenius's juvenile enthusiasm was irresistible: with the aid of floods of Ostwaldian ink, the joke soon spread far outside. The mistake has been made in our own time, therefore we must admit the possibility of making it; but it is none the less difficult to understand how a man of van't Hoff's genius could possibly have been misled by the observation of a parallelism into the assumption of any actual resemblance between gaseous pressure and the peculiar conditions of stress in a solution.

Both in my address in 1885 to the Chemical Section of the British Association and in my communication to

the Royal Society in the following year (written before I had been able to procure Arrhenius's paper) I took definite exception to the ionic dissociation hypothesis, even in the mild form postulated by Clausius. I also took exception, in the most positive manner possible, to the Arrhenius hypothesis in several of the reports, published by the British Association between 1885 and 1890, of the committee appointed to consider Electrolysis in its Physical and Chemical Bearings. At Leeds, again, in the discussion on the theory of solution, I protested against the acceptance of the ionic equation

$$\overset{+}{H} + \overset{-}{Cl} + \overset{+}{K} + \overset{-}{OH} = \overset{+}{K} + \overset{-}{Cl} + H_2O$$

in the following terms:

Such a conclusion, although undoubtedly necessary and logical from the dissociationist's point of view, involved the admission that hydrogen chloride and water were compounds of a totally different order; that these two hydrides were so different that while that of chlorine underwent practically complete dissociation, that of oxygen remained practically unchanged. Chemists, however, were in the habit of teaching that chlorine and oxygen were comparable elements and the facts of chemistry appeared to afford the strongest evidence that hydrogen chloride and oxide were in all ways comparable compounds. Moreover, the behaviour of the two compounds at high temperatures afforded no grounds for any such belief in the instability of the one and the stability of the other.

To this Ostwald made reply as follows:

Professor Armstrong has declared that the dissociation theory of electrolytes is unacceptable to chemists. As far as I am aware, there exists nowhere a real contradiction between chemical *facts* and the dissociation theory

but this theory only runs against all the time-honoured *feelings* of chemists. As feelings, although very powerful things, are at least variable with time and custom, it is to be expected that they will change sooner or later. The time is not very long past when the assumption that, in the vapour of ammonium chloride, hydrochloric acid and ammonia, which have "so great an affinity for each other," should exist separately from one another, ran in quite the same manner against the feelings of chemists. Now we are accustomed to this conception and in the same manner in a year or two chemists will speak as quietly of the free ions as they now speak of the uncombined mixture of hydrochloric acid and ammonia in the gaseous state. . . .

Professor Armstrong has asked why water does not split into ions, while hydrogen chloride, a body similar to water, does. But has Professor Armstrong forgotten that liquid hydrogen chloride, like pure water, is an *insulator* for the electric current, as was found long ago by Gore, an observation afterwards confirmed by Bleekrode? It has been stated by F. Kohlrausch that at ordinary temperatures no pure liquid is a good electrolyte. The theory of Arrhenius is still in this point the only one which explains this strange fact; *pure liquids do not conduct, because their molecules have no space to resolve themselves into ions* [my italics].

It is therefore not improbable that water would conduct electrolytically if we could find a suitable solvent for it. An investigation in this direction would be of very great interest but not without grave difficulties.

In a postscript to the German edition of the Report of the Leeds discussion (*Zeits. phys. Chem.* 1891, 7, 418), Ostwald further contended that much greater differences than are apparent between hydrogen chloride and water are noticeable between compounds such as NCl_3 and PCl_5, N_2O_5 and P_2O_5, which are more closely related than are hydrogen chloride and oxide.

It has always appeared to me that, in quoting such examples, Ostwald made a particularly unhappy choice, as nitrogen chloride and nitric anhydride are extraordinarily unstable, whilst hydrogen chloride and oxide are *both* eminently stable. His reference to liquid hydrogen chloride being, like water, an insulator, was also inconsequent. Nothing could show more clearly how little chemical feeling he had at that time and how unable he was to read the *facts* of chemistry. Moreover, to cite the dissociation of ammonium chloride as in any way confirmatory of the view that hydrogen chloride is dissociated into its ions in aqueous solution is entirely unjustifiable, especially as ammonia is supposed to remain unaffected: the two cases offer no point of analogy. Twenty years ago, it was clear that a sharp distinction must be drawn between the valency of nitrogen in the ammonium compounds and its valency in ammonia—between pentad and triad nitrogen; all that has happened in the interval serves to confirm this view, especially the considerations advanced by Barlow and Pope in their several memoirs on the correlation of crystalline form with structure.

It is a striking fact that Helmholtz, notwithstanding his partiality to atomic charges of electricity, was disturbed by the liberties taken by the dissociationists. This is clear from the following passage in his life by Kœnigsberger (English translation, p. 340):

Nernst has thrown himself zealously into the newest applications of physical chemistry, as worked out by the Dutchman van't Hoff and advocated with great vigour by Professor Ostwald of Leipzig in his *Journal*. These theories have already proved to be of great practical utility and have led to a multitude of demonstrably correct conclusions, although they imply some arbitrary assumptions which do not seem to me to be proven. The

chemists, however, make use of this hypothesis [of the dissociation of a portion of the compound molecules of the dissolved salts] in order to form a clear conception of the processes and they must be allowed to do this after their fashion, since the whole extraordinary comprehensive system of organic chemistry has developed in the most irrational manner, always linked with sensory images, which could not possibly be legitimate in the form in which they are represented. There is a sound core in this whole movement, the application of thermodynamics to chemistry, which is much purer in Planck's work. But thermodynamic laws in their abstract form can only be grasped by rigidly trained mathematicians and are accordingly scarcely accessible to the people who want to do experiments on solutions and their vapour tensions, freezing points, heats of solution, etc.

The fact which Helmholtz did not sufficiently appreciate was that the men who were taking the liberties he deprecated were not chemists, at least in feeling—that they were men who had thrown chemistry to the winds and were proceeding on hypothetical let-it-be-granted principles. The physico-chemical school, in fact, has never been a school of chemists.

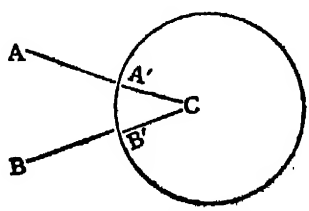
The one chief "nasty, ugly little fact" which has spoilt the dissociation hypothesis is the fact that the solvent has always been neglected by the advocates of the speculation. To Kohlrausch it was simply the screen serving to keep the ions apart. Ostwald at first preached a similar doctrine, arguing—as in the above quotation—that it gave space in which the dissociation could take place. In 1885 and again in 1886, as well as on several later occasions, I took exception to this view and insisted that solvent and solute were reciprocally affected. Gradually this was realised by the dissociationists but they quietly hedged and never had the grace to admit that ionic dissociation was not of the order of gaseous

dissociation—that the behaviour of hydrogen chloride was not that of ammonium chloride.

After 1893 my interpretation was paraphrased, in consequence of a suggestion made by J. J. Thomson and Nernst independently, that the cause of dissociation was the high specific inductive capacity of water. The attempt was then made to show that substances generally of high specific inductive capacity were active in promoting dissociation—but this turned out to be a signal failure in the main. The argument used by J. J. Thomson is of considerable interest (*Phil. Mag.* 1893, **36**, 320) :

The view that chemical action is electrolytic in character has been repeatedly urged by Prof. Armstrong. The ability of water to further this kind of action would be much greater if, while the chemical action were going on, the water existed in the liquid than it would if the water were in the gaseous state. If we take the view that the forces which hold the atom in the molecule together are electrical in their origin, it is evident that these forces will be very much diminished when the molecule is close to the surface of or surrounded by a conductor or a substance like water possessing a very large specific inductive capacity.

Then let AB represent two atoms in a molecule placed near a conducting sphere ; then the effect of the electricity induced in the sphere by A will be represented by an opposite charge placed at A′ the image of A in the sphere. If A is very near the surface of the sphere, then the



negative charge at A′ will be very nearly equal to that

at A. Thus the effect of the sphere will be practically to neutralise the electric effects of A; as but one of these effects is to hold the atom B in combination, the affinity between the atoms A and B will be almost annulled by the presence of the sphere. Molecules condensed on the surface of a sphere will thus be practically dissociated. The same effect would be produced if the molecules were surrounded by a substance possessing a very large specific inductive capacity. Since water is such a substance, it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in aqueous solution the forces between them are very much less than when the molecule is free and in the gaseous state.

The fallacy which underlies the application of this argument does not appear to have been recognised. It has not been sufficiently taken into account that the resolution of the compound A B into A and B under the influence of the water sphere is temporary only, in the sense that it obtains only while the two are in approximation. Their separation is apparent rather than real; in fact, the dissociation is merely potential and there would seem to be no reason why the superior osmotic effects which, *ex hypothesi*, are due to the *free* ions alone should be produced by them in the new state of restraint to which they are subject under the inductive influence.

Apart from the objection that the conception of ionic dissociation is opposed to reason and chemical common sense, there are other specific objections which appear to render the hypothesis untenable. "L'activité chimique se confonde avec l'activité electrolytique" is the expression used by Arrhenius in 1883; it has misled his followers to the present day. It is true only as regards the order of activity in a series of acids, for example; it is the reverse of true when the comparison is made for

various degrees of dilution: it then appears that whilst molecular conductivity increases on dilution, the very opposite is true of hydrolytic activity. The case is one like that propounded by the Duchess when she said, "The more there is of mine, the less there is of yours." If free ions increase in number as a solution is diluted and determine an increased conductivity, if these same ions determine hydrolytic activity, then hydrolytic activity must be directly proportional to the number of free ions. The argument is the same as that favoured by the thermodynamic school, when they confound you by proving that change of a certain character would involve perpetual motion—"which is impossible."

The rigidly selective action of enzymes as hydrolytic catalysts is in no way explicable by the ionic dissociation hypothesis—hydrogen ions, which, *ex hypothesi*, are the active agents in hydrolysis, cannot be supposed to act selectively.

Another and the most forcible of all arguments perhaps against the hypothesis is the proof which has been given, in case after case, by Brereton Baker and others, that the occurrence of chemical change is dependent not on dissociation but on the association in one conducting system of at least three components, one of which is an electrolyte.

Another argument is the preposterous limitation which the hypothesis imposes on our ability to explain chemical change, as it is only applicable to electrolytes, not to the vast host of organic compounds excepting organic acids and alkalies.

But what has weighed more than almost any other consideration with me has always been the absolute and uncompromising attitude of objection to the hypothesis taken by Fitzgerald at British Association meetings and especially in his Helmholtz Memorial Lecture. He alone

appeared to me always to understand the situation and to appreciate the difficulties.

The conceptions developed by van't Hoff, Arrhenius and Ostwald were never applicable to any but the weakest solutions. Strangely enough, these leaders of the movement elected from the beginning to sail under the flag which has been so aggressively waved by Sir Victor Horsley of late and made their grog by dipping only the wetted stopper of the spirit bottle into a tumblerful of water. And over and over again they and their followers made the mistake of considering only the volume of the solution as a whole; consequently they always went wrong when dealing with concentrated solutions. No two moderately concentrated solutions prepared by their method were of comparable strength.

Daylight was first let into the subject when Morse and Frazer showed that simple and consistent results were arrived at, even in the case of concentrated solutions, by dealing always with a definite mass of water and varying the proportion of solute—by using weight-normal solutions, as they are now termed. Independently I introduced the same practice into my laboratory and gave my reasons for so doing in June 1906 in a communication to the Royal Society on the "Origin of Osmotic Effects."

But how is the *thirst* of salted water—the superior activity of composite electrolytes generally—to be explained, if not by the assumption that the solute is dissociated into ions? The expression "thirst" is used advisedly, as being far more appropriate than the term "osmotic pressure," as the thirst experienced, for example, after eating salt junk is that engendered by the intrusion of salt into the water in the cells of the organism. The thirst originates in the salted water.

In 1885 and 1886 I insisted that both constituents of

the composite electrolyte, water as well as salt, acted reciprocally; this view I have never departed from. The idea has constantly been present in my mind that the act of dissolution involves some form of conjunction —yet not hydration as commonly understood. I made this quite clear in 1887 in the British Association report on electrolysis, where the following statement will be found:

> Nor do I conceive that it helps us to assume that a compound of hydrogen chloride with water is formed: it does not appear to me to be probable that an aggregate of the form $(HCl)(OH_2)_x$ would be more susceptible of electrolysis than the component simple molecules and that these would be more likely to suffer dissociation when associated than when free.

My work has so often been referred to in conjunction with that of Pickering on the determination of the composition of hydrates in solutions that it is desirable to point out that the questions considered by us were of a very different character. I always believed in the existence of hydrates but I was in search of something more—of a process, in fact, to account for the reciprocal character of the effect which solute and solvent exercised; one which at the same time would make it possible also to explain the effects produced by non-electrolytes. The explanation suddenly flashed into being after the discussion on ions in the Physical Section of the British Association in Bradford in 1900, the last occasion on which we enjoyed Fitzgerald's stimulating presence.

Taking into account the effect produced on water by a substance such as alcohol, for example (in lowering the freezing-point, etc.), as the extent to which such a substance could be supposed to exert a "dehydrating" action was very limited, it appeared obvious that its

action must be "mechanical" rather than chemical; consequently, that the real change must be in the water. A simple solution of the problem would be given, if it were supposed that water is a mixture of molecules of different orders of complexity, in equilibrium—a mixture of simple hydrone (OH_2) molecules with "polyhydrones" of various orders of complexity (see the previous chapter). The intrusion even of an entirely neutral substance (provided it were soluble) into such an assemblage would disturb the equilibrium in the direction represented by the generalised equation:

$$(HO_2)_x \rightarrow xOH_2$$

and the extent of the disturbance—the extent to which the polyhydrones would be dissociated—would depend on the number of individual neutral molecules introduced. To restore equilibrium in the direction

$$(OH_2)_x \leftarrow xOH_2$$

it would be necessary to cool such a solution more or less below the temperature at which ice would separate from pure water. The boiling point of the solution would be higher than that of water because of the presence of a larger proportion of *attractive* hydrone molecules and of molecules of the simpler polyhydrones. "Thirst" of hydrone would be conditioned in such a solution by the presence of an increased proportion of attractive hydrone molecules seeking to form water. The properties of aqueous solutions of non-electrolytes were thus referred to the fact that molecules of "Fair Hydrone" are eminently attractive of their own kind.

It thus became obvious that the method adopted by van't Hoff and others of using volume-normal solutions

must be a fallacious one, except in the case of very dilute solutions, owing to the great variation in the relative molecular proportions of solvent and solute in such solutions, a substance of small molecular weight (such as alcohol) displacing but little water, one of high molecular weight (such as cane sugar) a large amount. It was clear that the solvent was the test substance—that all thought of analogy with the gaseous state must be put aside and the effect ascertained of this and that substance on this and that property of some definite mass of the liquid. Raoult's work, for example, had been done from such a rational point of view; its real significance had been obscured, however, by the use of a false analogy.

It became necessary to revise the data relating to concentrated solutions from this point of view and especially to examine acids and salts under comparable conditions. The work carried out in my laboratory during the past few years has afforded material for what appears to be a rational explanation of the behaviour of substances the solutions of which behave as electrolytes. The assumption made is that the formation of composite electrolytes by the dissolution in water of substances such as the acids, the alkalies and salts generally, is a process involving the *distribution* of both constituents of the composite electrolyte—thus:

$$HCl + OH_2 \longleftrightarrow HCl\left\langle{}^{H}_{OH}\right.$$

$$H_2O + ClH \longleftrightarrow H_2O\left\langle{}^{Cl}_{H}\right.$$

and that the occurrence of electrolysis involves the interaction of the two kinds of complex while under the influence of an electromotive force. The extent to which

this distribution occurs determines the activity of the composite electrolyte.

In the case of non-electrolytes, it is to be assumed that only the water is distributed, thus:

$$\begin{matrix} C_2H_5 \\ H \end{matrix}\!\!>\!O + OH_2 \longleftrightarrow \begin{matrix} C_2H_5 \\ H \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} H \\ OH \end{matrix}$$

The superior activity of salts, etc., in disturbing the properties of water is due to the fact that besides acting mechanically, they also exercise an attractive effect of their own; in the case of a solution of hydrogen chloride, for example, the $HCl\!<\!\!\begin{matrix} H \\ OH \end{matrix}$ complex in virtue of the presence of the OH radicle, the $H_2O\!<\!\!\begin{matrix} H \\ Cl \end{matrix}$ complex in virtue of the presence of the Cl radicle, would both be active in much the same way that the hydrone molecule in water is active.

A completely distributed binary molecule AB would therefore exercise the effect of two molecules in disturbing the properties of the water. The further consequences of this hypothesis must be painted on another occasion. [This conclusion is corrected later on. See p. 259.]

My story has a moral. It is well known that the dissociation hypothesis dealt with in this essay has attained to an extraordinary popularity; this is in no way surprising, as chemical activity is a subject in which so many are interested.

All the major channels of communication and most of the minor are secured by the high priests of the cult: they command the almost universal obedience of student youth and now their technical jargon confronts us everywhere. Thus, recently, when recovering from an indisposition, happening to take a mild course of Pharmacology,

turning over the pages of a standard text-book on the subject under "Acids" I came across the following explanation of the various physiological effects which they produce:

> In all these effects mineral acids are much more active than organic acids . . . the difference in action is solely one of dissociation. All acids have an antiseptic action which varies with the dissociation, that is, the number of H ions in the solution.

This is but typical of the kind of statement constantly met with. It is either very learned talk in the mystic language of the initiate or misleading undiluted piffle—I should say the latter. The seriousness of the situation such language creates, however, lies in the fact that it is directed to those who later on will be responsible for the lives of men, who should grow up with clear ideas, to reverence science and to put trust in its votaries.

It will be held by some, perhaps, even by many, that even if my indictment be true, it matters little nevertheless that a visionary scheme has been advanced—or even that it should have been forced into use for a time. It has inspired workers.

If so, however, at what expense of truth has victory been gained—if indeed there be true victory of any kind? What nature of example is it that we have set? To what extent are almost all sources of information available to the youthful mind polluted for years to come?

It is difficult to avoid the conclusion that we have offended against all the old canons of practice by which former workers were guided. They disputed, often vigorously and violently—they held the strongest opinions but, as a rule, they were careful to balance arguments and to allow arguments to be balanced.

The modern method is not even to present the case of the opponent—the student is not allowed the choice of alternatives, he is rarely, if ever, informed that there are alternatives. Prof. J—— simply asserts: "This is truth; believe it you must and shall." Of such kind has been the Leipzig message from the beginning. The spirit of intolerance is abroad among us. If we are not almost back to the days of the Inquisition, we are at least as dogmatic as are the adherents of any religious persuasion. All this in the sacred name of science and of scientific method, of the discipline upon which we are placing so much hope of future enlightenment of society!

A large proportion of those who are being taught on such lines will become teachers in the future—the result must be disastrous; indeed, we can see already that such is the case. In the main the teaching of science is a failure, not only in our universities but also in our schools. The hopes formed by men like Charles Kingsley, Herbert Spencer, Huxley, Tyndall are in no way being fulfilled. So little true scientific method is taught—the great lessons of truth to be learnt by the study of science, of which Kingsley speaks with such rare eloquence in his volume of *Scientific Essays*, is in no way brought properly before the notice of scholars.

The ideal philosopher contemplated by Faraday was one who pursues inquiry "zealously and cautiously, combining experiment with analogy, suspicious of preconceived notions, paying more respect to a fact than a theory, not too hasty to generalise and, above all things, willing at every step to cross-examine his own opinions both by reasoning and experiments." This ideal is that which Faraday himself always had in mind, which gave to his work its incomparable value. We later workers may well strive to follow him.

The history of the development of the ionic dissociation hypothesis appears to me to be one of gravest warning, which we should heed before it be too late: the great ethical value of the lessons to be derived from it should not be overlooked.

1911

THE CORROSION OF IRON AND OTHER METALS*

"But though such is my view, I put it forth with all the reservation made on former occasions. I do not pretend to explain all points of difficulty. . . . I profess rather to point out the difficulties in the way of the views which are at present somewhat too easily accepted and to shake men's minds from their habitual trust in them; for next to developing and expounding that appears to me the most useful and effectual way of really advancing the subject:—it is better to be aware or even to suspect we are wrong than to be unconsciously or easily led to accept an error as right."

FARADAY, *On Some Points of Magnetic Philosophy*, 1854.

ON account of the ever-increasing use that is made of steel not only in constructing machinery, rail- and tramways, bridges and ships of every kind but also as the framework of buildings often of huge dimensions, it is most important that engineers and all who are responsible for the care of iron and steel structures should be fully

* *The Corrosion and Preservation of Iron and Steel.* By Allerton S. Cushman, A.M., Ph.D., and Henry A. Gardner. (McGraw-Hill Book Co., 6, Bouverie Street, London, E.C. 1910. Price 17*s.*)—"The Corrosion of Iron and Steel." By W. H. Walker, A. M. Cederholm, and L. N. Bent, *Journ. Amer. Chem. Soc.* 1907, 25, 394—"The Rusting of Iron." By William Augustus Tilden, *Chem. Soc. Trans.* 1908, 1365—"The Rusting of Iron." By J. Newton Friend, *Journ. of the Iron and Steel Institute*, 1908, No. 11—"The Preservation of Iron and Steel." By A. S. Cushman. "The Electrolytic Theory of the Corrosion of Iron and its Applications." By W. H. Walker (with discussion), *ibid*, 1909, No. 1—"The Rusting of Iron." By J. Newton Friend, *Chem. Soc. Proc.* 1910, 179—"The Wet Oxidation of Metals: I. The Rusting of Iron." By Bertram Lambert and J. C. Thomson, *Chem. Soc. Trans.* 1910, 2426.

alive to the conditions under which rusting takes place and to the precautions that must be taken if the metal is to be preserved from decay. The subject was discussed in this Journal in 1907, in the January number, with reference to experiments carried out by Dr. G. T. Moody, whose results had been made public in the previous year. In the interval the conclusion Moody arrived at that rusting is necessarily and always *primarily* conditioned by the presence of acid has either been challenged by more than one observer or the issue obscured by the introduction of other considerations. It therefore appears to be desirable to reopen the discussion from this point of view and to consider the cogency of the arguments advanced, especially as Moody's contention is not accepted by Messrs. Cushman and Gardner in their recent comprehensive book on the subject of the corrosion of metals, a work which will doubtless be regarded by engineers and builders as authoritative on account of the position one of its authors occupies in the United States Department of Agriculture and the attention he appears to have given to the subject.

The historian of the future considering the growth of scientific knowledge during the latter half of the nineteenth century will be sorely puzzled probably to account for the slowness with which chemists arrived at clear conceptions of the nature of chemical change and of the conditions that determine it. Perhaps he will be forced to conclude that it is not within the compass of average human nature to be scientific—that dogma must necessarily be preferred above science. It is certainly strange that a problem of such importance as that afforded by the rusting of iron should be a subject on which opinions can differ to the extent apparent in recent discussions.

If the conditions that determine the attack of metals are to be appreciated, there are certain fundamental facts upon which, in the first instance, attention should be centred.

When common spelter—the crude zinc of commerce—is placed in dilute sulphuric or muriatic acid, it is at once attacked and dissolved. In most text-books the interaction is represented, without further remark, by the expression:

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

The student is allowed to believe that the metal actually displaces hydrogen from the acid; usually no account is taken of the part played by the impurities in the zinc. But as zinc is freed from the impurities which are associated with it in spelter—arsenic, lead, graphite, etc.—it becomes less and less readily attackable by acids and ultimately all but insoluble. All who have worked with carefully purified material agree that this is the case: for example, Lieut.-Colonel Reynolds and Professor Ramsay (*Chem. Soc. Trans.* 1887, **51**, 857) in speaking of a specimen of the metal which they had separated from most carefully purified zinc sulphate by electrolysis and then volatilised in an exhausted tube of hard glass, say: "The sublimed metal appeared to be so pure that it was nearly unacted on by sulphuric or hydrochloric acid."

Such is the experience of every one who has had occasion to purify zinc. It is only logical to assume therefore that zinc *pure and simple* would not be attacked by such acids.

It may be desirable to insist here that a pure material must ever remain an abstraction, taking into account the fact that any and every substance is necessarily in some

degree subject during its preparation to contamination by its environment.

It has long been known that even highly impure zinc may be "protected" by amalgamation with mercury, that is to say, by rubbing this metal over the surface of the zinc after it has been a short time exposed to the action of acid. The property is one of extreme value and is shared with zinc by no other metal except the allied element cadmium—hence it is that amalgamated zinc was so long made use of in voltaic batteries instead of the cheaper iron, which approaches zinc in electromotive efficiency.

Faraday explained the effect of impurities in the zinc in causing it to dissolve in acid in the following lucid terms (*Experimental Researches in Electricity*, 1834, Series VIII, § 998).

"The cause is, that when ordinary zinc is acted upon by dilute sulphuric acid, portions of copper, lead, cadmium or other metals which it may contain are set free upon its surface; and these, being in contact with the zinc, form small but very active voltaic circles, which cause great destruction of the zinc and evolution of hydrogen, apparently upon the zinc surface but really upon the surface of these incidental metals. In the same proportion as they serve to discharge or convey the electricity back to the zinc do they diminish its power of producing an electric current which shall extend to a greater distance across the acid and be discharged only through the copper or platina plate which is associated with it for the purpose of forming a voltaic apparatus."

The explanation Faraday gave of the effect of amalgamation is as follows (*ibid.* § 1000):

"It is probable that the mercury acts by bringing the

surface, in consequence of its fluidity, into one uniform condition and preventing those differences in character between one spot and another which are necessary for the formation of the minute voltaic circuits referred to. If any difference does exist at the first moment, with regard to the proportion of zinc and mercury, at one spot on the *surface* as compared with another, that spot having the least mercury is first acted upon and, by solution of the zinc, is soon placed in the same condition as the other parts and the whole plate rendered superficially uniform. One part cannot therefore act as a discharger to another; and hence *all* the chemical power upon the water at its surface is in that equable condition which, though it tends to produce an electric current through the liquid to another plate of metal which can act as a discharger, presents no irregularities by which any one part, having weaker affinities for oxygen, can act as a discharger to another."

No better explanation has yet been advanced. We are still content to think of the zinc surface as reduced to "an equable condition"; whatever the explanation, the effect produced is very remarkable.

Although the presence of mercury serves to protect the zinc against acid, action sets in immediately the amalgamated surface is touched by any "metallic" conductor relatively negative to zinc. It is not improbable that the zinc is protected because it is covered with a liquid film of a saturated solution of zinc in mercury so constituted that the uppermost layer consists of mercury only, much as an aqueous solution may be thought of as covered with a tenuous film of pure water; the electropositive zinc may be thought of as brought to the surface immediately contact is made with the relatively electronegative conductor: then as being at once gripped by the acid radicle and drawn into solution.

The essential act by which attack is determined is the

formation of a conducting circuit of three components, two being metals, the third an acid ; all are conductors of electricity but one of them, the acid solution, is decomposed or electrolysed in conducting—that is to say, it is an electrolyte. These are the conditions apparently that obtain in any and every case of chemical change—in other words, the occurrence of chemical change is dependent on the production of an electric current but this current is only produced as the change is consummated : the two phenomena are interdependent and inseparable. Such may be said to be the electrolytic theory of chemical change—the theory being that change only takes place when, to use Faraday's words, "active voltaic circles" are formed.

The evidence brought forward in support of this view during the past five-and-twenty years is remarkably complete and cannot well be gainsaid. In case after case it has been shown that the implication constantly set before students of chemistry that combination or interaction takes place between two compounds A and B is incorrect and that in all instances, to promote change, a third substance must be coupled with these, the third "substance" being of such nature that, if not itself a electrolyte, it is one from which an electrolyte is produced by association with either A or B, the presence of an electrolyte being an essential feature in the occurrence of change.

The student is invariably told that oxygen is a supporter of combustion and is led to think that oxygen and the burning substance are the two factors in the process. As a matter of fact, carefully dried carbon and phosphorus do not burn in carefully dried oxygen ; they will take fire only in the moist gas. Although ammonia and hydrogen chloride prepared in the ordinary way combine with the greatest readiness, forming solid ammonium chloride, if

very special care be taken to dry both gases nothing happens when they are mixed.

Again, an ordinary mixture of hydrogen and oxygen is exploded with the greatest readiness but if prepared with special care by electrolysing an alkaline solution of baryta, so that it contains no trace of acid, the mixture, even if dried simply by freezing out water from it by means of liquid air, is no longer explosive. A coil of silver wire may be heated to redness in the dried mixture without firing it—yet liquid water gradually makes its appearance, the interaction taking place slowly and without explosive violence. This result is one of the very greatest importance, as it is a proof that the presence of water is not in itself sufficient to bring about the change : nor should it be, from the electrolytic point of view advocated above, as water is not an electrolyte; only "dirty" water behaves as an electrolyte—that is to say, water containing some substance dissolved in it—a trace of an acid, of an alkali or of a salt, as the case may require. There can be little if any doubt that in cases in which moisture alone has been observed to condition change, it is because traces of "impurity" were present together with water ; obviously it is impossible to avoid such and it must therefore always be impossible to prevent a change such as that involved in the formation of water from the elementary gases hydrogen and oxygen from taking place to some slight extent.

It would be ungracious to pass from this subject without referring to the great debt which chemists owe to Dr. Brereton Baker for his work on highly purified materials—work which he has carried on with unwearied perseverance and with a degree of skill that appears to be altogether peculiar to himself. Strangely enough, such work has only been done in this country and but little attention has been paid to the subject elsewhere ;

the significance of Baker's results in relation to the problems of chemical change is certainly in no way properly appreciated at present.

In the discussion that has taken place since the results of Moody's experiments were made known, it has not been denied that iron dissolves in presence of the carbonic acid which is necessarily present in ordinary water and in the film of water which condenses on the surface of the metal whenever it is exposed in a moist atmosphere at a sufficiently low temperature. What is asserted is that corrosion may and does take place in the absence of carbonic or any other acid. This assertion may be considered from two points of view—firstly, with reference to the observations on which it is based : that is to say, with reference to the facts ; secondly, from the point of view of the hypothesis by which it is supported.

The character of the evidence put forward will be best understood if a few quotations be given from Cushman and Gardner's work descriptive of experiments affording results which they claim are proof that iron is dissolved without the intervention of acid and that rusting may be conditioned by water and oxygen alone :

"The two clean Jena flasks A and B are three-quarters filled with pure freshly distilled water. Two drops of an alcoholic solution of phenolphthalein indicator (1 gram in 100 cc. pure alcohol) are added to the water in each of the flasks. The beaker C is more capacious than the flasks A and B. The flasks D and E are used in each experiment as blanks to check the results obtained. After connecting up as shown, the water in each vessel is simultaneously boiled very vigorously until about one-quarter is boiled off. The rubber stopper in A is then lifted and clean, polished strips of iron quickly slipped in. The stopper is again tightly inserted and the

boiling continued for about fifteen minutes. The lamps under A and E are then extinguished, while the water in B, C and D continues to boil. As soon as flasks A and E have sucked back the boiling water so that they are completely filled, the lamps under flasks B and D are also extinguished. When B is quite full, flasks A and B are quickly cooled by surrounding them with cold water. The valve at F is then closed. By this means the bright specimens are immersed in water practically free from air, oxygen or carbonic acid and may be kept under observation for any desired length of time. This experiment has been repeated a great number of times with different samples of iron and steel and no rusting has ever been observed unless air was allowed to enter."

"It has been shown that the electrolytic theory of the wet oxidation of iron is based on the premise that iron must first go into solution, an equivalent amount of hydrogen being set free. The resulting ferrous hydroxide

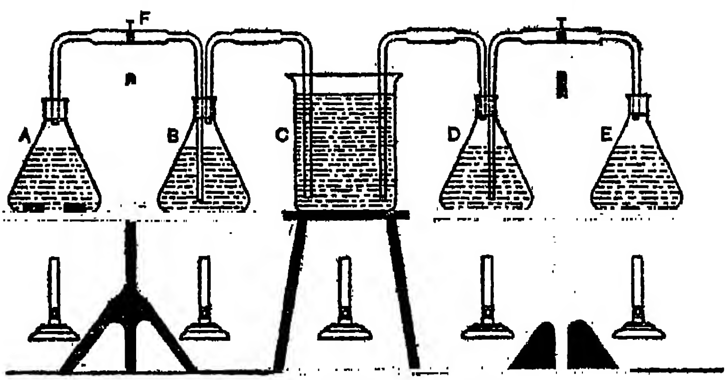


FIG. 1.

in solution betrays its presence by producing a pink coloration with the phenolphthalein indicator. In every experiment made the pink colour was seen, although in some cases the colour developed slowly and only after the lapse of a number of hours. That the colour was not due to the action of water on the Jena glass is shown by

the fact that no colour appeared on the blank side of the experiments."

In other words, it is argued by Cushman and Gardner that a certain amount of iron was dissolved and that it was dissolved by the action of water alone. Further proof that iron had been dissolved is given by their statement made with reference to other similar experiments that on allowing oxygen carefully purified from carbonic acid to bubble through the flasks rust appeared on the bright metal surfaces in five minutes or less and in one hour was deep and heavy.

There is no reason to dispute the conclusion arrived at by Cushman and Gardner that whilst some iron is dissolved no rusting takes place under conditions such as were realised in their experiments until oxygen was admitted: it may well be that boiling the water in the manner described would have the effect of so nearly removing the whole of the oxygen dissolved in the water that there should be no obvious rusting under such conditions. It is known, however, that the complete displacement of carbon dioxide from water is a very difficult task, if not an impossibility; it cannot be admitted that the treatment described would be effective in removing it entirely.

Cushman and Gardner themselves admit that it may be doubted whether it is possible to boil out all carbonic acid from the water contained in the apparatus described. They contend, however, that "granting this is the case in regard to the last traces, it is easily shown that the hydrogen ions which would be supplied by a minute quantity of carbonic acid are of no more importance than the hydrogen ions supplied by the normal dissociation of pure water and that the assumption that carbonic acid must be present is quite unnecessary."

They then call attention to Whitney's argument that the concentration of "hydrogen ions" in a solution of carbon dioxide in equilibrium with ordinary air at 15° is 16 grams per 10,000,000 litres of water—"or only sixteen times as many as perfectly pure water contains; and that, at the boiling temperature, the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than in pure water, for not only is the solubility of the gas greatly diminished but the dissociation of water is greatly increased by rise of temperature."

We are here brought into the region of pure speculation, not to say obfuscation; a definite issue is raised, however, that can be discussed.

Nothing could be more complete than the following statement by Dr. Cushman:

"It appears to the writer to be demonstrated that Whitney was right in his assertion that iron goes into solution up to a certain maximum concentration in pure water without the aid of oxygen, carbonic acid or other reacting substances.

"*Rusting of Iron primarily due to Attack by Hydrogen Ions.*—This point established, it becomes apparent that the rusting of iron is primarily due *not to attack by oxygen but by hydrogen ions.*"

In the interest of engineers and others not versed in the scientific jargon of the day, who wish to have explanations given in plain terms, it is clearly desirable to consider what is meant by such statements.

The cult of the free and independent ion has so dominated most branches of physical and biological science during the past twenty-five years that it may almost be ranked with influenza and plague as one of the infectious complaints that have been brought into

prominence in modern times. The manner of its development is very remarkable.

Having made the fundamental discovery that compound substances which are decomposed by an electric current are resolved into two parts, Faraday in 1834 coined the word *ion* simply to express "those bodies which can pass to the electrodes in electrolysis."

It was not until 1857 that Clausius postulated the conception that probably some of the encounters that take place between the moving compound molecules in a liquid are so violent that some of the molecules are broken up into their constituent atoms. To explain electrolysis, he assumed that when an electromotive force is applied to a liquid it does not produce disruptions and reunions but finding these already going on influences the motions of the parts during their intervals of freedom, so that the positive move more in the positive direction and the negative move more in the negative direction than would be the case if they were uninfluenced. Clausius apparently did not suppose that compounds were broken up only into their ions; indeed, on his kinetic hypothesis it is difficult to see why all of the atoms in a compound should not make their separate appearance at the electrodes—why all compounds which undergo electrolysis should always be broken up in a particular way into two ions only, the one being always hydrogen or a metal, the other whatever is associated with the hydrogen or metal in the compound; furthermore why so many compounds—organic compounds in particular—should not be in the least affected by an electric current. The fact that, in so many cases, when substances are mixed which by themselves have no electrical conducting power, solutions are obtained which conduct readily is also in no way accounted for by the hypothesis.

In 1884, without considering any of the difficulties inherent in the Clausius hypothesis, Arrhenius put forward the proposition that not only was the conductivity of solutions to be ascribed to the presence in them of the dissociated, electrically charged *ions* of the dissolved substance but that it was proportional to the degree of dissociation and he assumed that the dissociation was practically complete in dilute solutions of strong acids. He recognised, moreover, that there was a close correspondence between chemical activity and electrical conductivity in the case of acids; in fact, his conclusions were summarised in the pregnant sentence: "L'activité électrolytique se confonde avec l'activité chimique."

The conclusions at which Arrhenius arrived were so fascinating and the correlation of chemical with physical activity was so welcome, that the hearts of chemists were captured forthwith; it was a case of unreflecting love at first sight. The fact was overlooked that the solvent was in no way taken into account; the violence of the assumption made in supposing that practically all of the molecules of the dissolved substance "went smash" while those of the solvent remained unaffected was not remarked. To the present day, conductivity is very generally ascribed to the presence of free dissociated ions and to these alone.

After this digression, consideration of Cushman and Gardner's argument may be resumed. Having stated that three "theories" of rusting are to be considered: (1) The carbonic acid theory; (2) the peroxide theory; (3) the electrolytic theory, they proceed to dismiss (1) and (2) on various grounds, and then state the third in the following terms:

The Electrolytic Theory.—From the standpoint of the modern theory of solutions, all reactions which take place

in the wet way are attended with certain readjustment of the electrical states of the reacting ions. The electrolytic theory of rusting assumes that before iron can oxidise in the wet way it must first pass into solution as a ferrous iron. The subject has been interestingly treated by Whitney, who discussed it from the standpoint of Nernst's conception of the source of electromotive force between a metal and a solution. When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal and is electrolytically classed with copper in relation to iron. If, therefore, we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron and, therefore, its subsequent oxidation, must be accompanied by a 'precipitation' or setting free of hydrogen. It is very well known that solutions of ferrous salts, as well as freshly precipitated ferrous hydroxide, are rapidly oxidised by the free oxygen of the air to the ferric conditions, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one.

Pure Water a Solvent of Iron.—As iron has been shown by Whitney, Dunstan and one of the authors, to rust in the presence of pure water and oxygen alone, the electrolytic theory as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, viz., Does iron pass into solution, even to the slightest extent, in pure water? If iron does dissolve, the electrolytic theory is so far satisfactory; if it does not dissolve, we must conclude that the oxygen finds some way of directly attacking the metal.

"Almost every one will admit that in the case of

impure iron, with its unhomogeneous physical and chemical constitution, electrolysis will supervene but it must be remembered that we are now concerned with the underlying cause of the wet oxidation or hydroxylation of iron, regardless of its state of chemical purity.

"According to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 gram in 10,000,000 litres. If iron dissolves in the purest water it should be by interchange with hydrogen and as Whitney has pointed out, pure water is to this extent an acid."

Then follows an account of experiments such as have been referred to, showing that no rusting took place in boiled-out water until oxygen was admitted, although iron had been dissolved prior to the entry of the oxygen. It will not be easy for the average reader interested in the problem under discussion to disentangle the meaning from the quotation just given. The implication is firstly that *pure water* (H_2O) is to some extent "dissociated" or resolved into the ions H and OH and that when iron is placed in contact with *pure* water iron atoms or ions enter into solution in exchange for the hydrogen ions, hence the appearance of iron in the solution in the experiments referred to.

The answer to these contentions is that no one has yet dealt with *pure* water and that it is practically inconceivable that anyone ever should.

What has been done is to take ordinary water and purify it, after boiling out dissolved volatile "impurities," by repeated distillation *in glass vessels*: as purification proceeds, the power of the liquid to conduct an electric current diminishes and becomes very, very slight; it is only logical to assume that if pure water could be obtained, *i.e.* water free from every other substance, it would have no conducting power. As even the hardest

glass is to some slight extent attacked by water, it is inconceivable that pure water should ever be obtained at all events by the use of glass vessels; and if vessels, say of iridium—the least attackable of metals—were used, there would still be the difficulty, again all but insuperable if not entirely so, of getting rid of surface impurities derived from the environment during working. The conductivity test is of such delicacy that the most minute impurity tells.

No "electrolytic theory" can apply to water if water be a non-conductor, the essence of the electrolytic theory being that action takes place because an electrolyte is present which is resolved by the passage of the current through it into its ions, one of which at least is active towards the electrode at which it is delivered.

That two substances, such as iron and water, neither being an electrolyte, should interact (without the intervention of a third) is improbable, to say the least, also for another reason. When two conductors are brought into contact, it is well known that they are at a different electrical potential at the junction: years ago there was much discussion as to the origin of this difference—whether it might be regarded as an actual contact difference or whether it should not be supposed that some minute amount of chemical change took place at the junction in which a film of moisture condensed on the surfaces brought into contact was concerned. The question has never been settled and there are almost insuperable difficulties in the way of settling it experimentally. Assuming that such an electrical difference exists at the junction of two substances, on joining them at the other extremity an equal but oppositely directed difference of potential would be developed: consequently, a circuit could not be established in which an electric current would flow. To secure a flow of current, the introduction

of a third component into the system is required to afford the necessary slope of potential.

For the various reasons given it may be contended therefore that the answer to Dr. Cushman's "one crucial question"—"Does iron pass into solution, even to the slightest extent, in pure water?"—must be, on the practical side at least: "That it is not proven that it does"; on the theoretical: "That it is highly improbable that it does, not to say impossible that it should." Or perhaps it should be said, as it cannot be denied that, strictly speaking, no substance is insoluble in water, that if iron dissolved it would dissolve mechanically in the water and in the absence of acids it would not rust, even if oxygen were present. But such an ideal condition of purity is only conceivable; it could not be realised.

Taking Moody's and Friend's observations into account, it may be said to be proved that whenever iron is dissolved acid is present and active. Objection has been taken to Moody's conclusion on the ground that the inactivity of the iron he used towards water was due to the fact that by cleaning the iron in chromic acid before exposing it to oxygen and water he rendered it *passive*—but the account he gives is full of proof to the contrary. Thus he states that rusting began when ordinary air was allowed to enter into the tubes in which iron had been exposed during long periods in contact with purified air and water without any rusting being apparent; also that the iron at once began to rust when and where it came into contact with the glass tube in which it was enclosed. I still have in my possession tubes prepared by Moody several years ago in which iron is sealed up in contact with water and oxygen and not the least rusting is apparent, except at one spot where, owing to careless handling by students, the V-shaped tube having been turned upside down, the iron rod was allowed to come into contact with the glass

and to remain in contact with it during a short time. Friend has also observed that contact with glass promotes rusting. This observation is in itself most significant as showing the influence that acids have in promoting rusting—the effect cannot well be ascribed to any other cause than to the action of silicic acid present at the glass surface.

Friend, however, has met the criticism applied to Moody's results in a most ingenious way, by carrying out experiments with the simple apparatus shown in fig. 2.

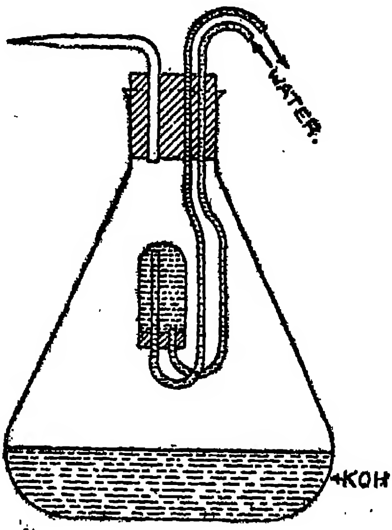


FIG. 2.

The thimble-shaped tube shown within the flask is of iron and can be cooled by circulating water inside it in the manner indicated; the flask contains strong caustic potash solution and above this air. At the outset, some of the air is expelled or withdrawn and the flask closed by sealing the side-tube at its point; after shaking well, so as to wash down all the surfaces exposed within the

flask with alkali, to remove all traces of adherent carbonic acid, the flask is immersed in water at 100° and cold water circulated through the iron thimble; as the steam condenses on the outer iron surface, this becomes cleansed of alkali; when the cleansing process is judged to be complete, the flask is set aside. Operating in this way, Friend found that no rusting took place, except on one occasion when a couple of rust spots were formed at the top of the thimble; as the spots appeared at the same place after the rust had been removed, there can be no doubt that the rusting was due to the presence of "slag" at the point affected. Moody had a similar experience and advisedly used chromic acid as a means of removing manganese sulphide—a common impurity in iron, which apparently undergoes oxidation with particular readiness, giving rise to acid. It should be added that Friend cleaned the iron he used by mechanical means and assured himself at the close of each experiment that the alkali had been washed off the surface.

Taken in conjunction with Moody's experiments, Friend's observations afford the clearest possible proof that the presence of acid is essential to rusting. The results obtained by others which appear to contravene their conclusions can only be ascribed to lack of success in effecting the complete removal either of carbonic acid or of slag from the iron.

It is quite clear that the engineer and builder need not concern themselves in the very slightest with ions—least of all whether they enjoy independent existence or not in solution: this may well be left a subject of academic dispute; indeed the proper protection of iron against decay is of such supreme public importance that any attempt to complicate the problem by the introduction of a pretentious jargon, which even the expert can

fathom with difficulty and which serves mainly to cloak ignorance, deserves to be visited with the most absolute disapproval. Suffice it for the engineer to know that, in the first place, he should "keep his powder dry"—in other words, he should take every possible precaution to prevent liquid films of water from collecting on iron surfaces, as such films necessarily contain carbonic acid in solution, carbon dioxide being present in the air at all times; secondly, that the access of acid to the iron is to be avoided on all occasions but more especially if the conditions be such that water can condense readily on the iron.

The extraordinary slowness with which ideas are spread and clear conceptions are arrived at is well illustrated by the publication recently by Messrs. Lambert and Thomson of an account of experiments on the oxidation of iron which they have carried out with the greatest perseverance and manipulative skill but obviously without any clear understanding of the conditions underlying the processes of chemical change and without any clear conception of the problems to be solved.

The aim of the investigation is said to have been "to bring together, under the simplest possible conditions, the purest obtainable water, oxygen and iron in vessels which would be least likely to be acted on by any of these substances."

Now, although it may be true that "to the pure all things are pure," to the chemist who thinks all things are impure and must ever remain so—some contamination is unavoidable; the important question to consider is whether or no a particular impurity can be counted as harmful. Pure is defined in the dictionary as—"separate from all heterogeneous or extraneous matter": a pure thing is the thing in itself. There can be no degrees of

purity—pure is to be qualified only by such words as "nearly," "far from," etc. At most, we can speak of "highly purified" or of "very nearly" or "all but pure" substances. Messrs. Lambert and Thomson misuse and misapply the word "pure" throughout their communication.

The results they have obtained show, they say:

"that chemically pure iron will not undergo visible oxidation even after long exposure to pure water and pure oxygen in vessels made of clear fused silica. Further, that a very small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions, where there is not the remotest chance of any acid substance either being present or being formed during the reaction."

It is worth while considering to what extent these statements are justified. "Chemically pure," unfortunately, is a phrase to which no precise meaning can be attached—it means a material purified by a chemist, whose degree of success will depend on the methods he may adopt in purifying the material. Messrs. Lambert and Thomson tell us that to prepare "pure iron" they took a "pure specimen" of ferric chloride from a certain dealer—at the best a very indefinite description. Metallic iron was separated from the salt by electrolysing it between iridium electrodes. The metal was then made into nitrate, the which salt was purified by recrystallisation from purified nitric acid; the salt thus obtained was colourless, whereas ferric nitrate prepared from "ordinary pure iron" is pale violet; this is probably the most interesting and valuable observation made in the course of the inquiry and is alone well worth all the trouble they expended on the preparation of the salt. Ultimately the nitrate was decomposed by heat and the

oxide reduced to metal by "pure hydrogen"—whether ordinary pure or chemically pure we are not told.

Iron so prepared was not visibly oxidised under the conditions arranged by Lambert and Thomson even after several months.

On the other hand, iron made in precisely the same way from "ordinary pure iron" invariably showed signs of oxidation in two or three hours. In like manner, when platinum vessels were used, particularly when a platinum boat was substituted for one made of iridium to contain the iron oxide (prepared from the most purified materials) while it was submitted to reduction in hydrogen, the iron produced underwent oxidation readily in two or three hours, rusting taking place invariably at those parts of the metal which had been heated in contact with the platinum tube. All kinds of commercial iron rusted readily in their apparatus; they even go so far as to state that commercial electrolytic sheet iron cleaned by Moody's method with chromic acid was readily attacked, thus disposing again of the contention that chromic acid necessarily renders iron passive.*

It is clear that Lambert and Thomson unwittingly arranged matters so that iron would rust in their apparatus *whenever it was coupled with the necessary electro-negative conductor*; by using iridium vessels, which apparently are not in the least subject to attack even by chlorine and strong acids, they were able to prepare an iron free from electro-negative impurity—as is to be expected on all grounds, such iron did not rust. This result is an interesting verification of the only theory of chemical change that is in accordance with present knowledge but it is nothing more. The work affords no disproof of Moody's argument; on the contrary, it supports it most strongly. There can be little doubt that although

* Compare Brereton Baker, *Chemical Society's Report*, 1910, p. 38.

Lambert and Thomson were successful in carrying the purification of iron very far, they were not sufficiently careful to secure the removal of carbon dioxide from their apparatus. In view of the results obtained by others, it is inconceivable that they would have arrived at results such as they describe had they done so. And it is not difficult to see where they went astray. Whilst they took great care to prepare oxygen free from acid impurity by electrolysing a solution of baryta and all water introduced into the apparatus was carefully distilled from an alkaline solution, they evidently were not alive to the difficulty of removing carbon dioxide entirely from glass surfaces, although this has long been recognised; a very large area of glass was exposed within their apparatus, especially in the vessel in which the oxygen was stored. A simple apparatus such as Friend used is in reality far better suited to such an inquiry than the highly complicated apparatus used by Lambert and Thomson. But simple conditions are usually adopted by all experimenters only as a last resort.

1922

FIRST MESSEL MEMORIAL LECTURE

RHAPSODIES CULLED FROM THE THIONIC EPOS

CHEMICAL CHANGE *AND* CATALYSIS

Semper aliquid certi proponendum est

WHEN this Address was undertaken—

> What did we do but make a vow
> To do we knew not what nor how? *

What should be my theme? I could not well round upon you, as I might have done upon the Brewers when addressing them last year, with the lines—

> Thou that with ale or viler liquors
> Didst inspire Withers, Pryn and Vicars
> And force them, tho' it was in spite
> Of Nature and their stars, to write,

unless, indeed, sulphuric acid were counted among "viler liquors," a course I would not advocate: in fact, I shall plead for it the place of Prince among them and

*American readers please note, the citations when not identified are from sources at least two centuries old.

ask that once more due honour be given to its might and solidarity.

Fortunately, you inspired me by a flashed vision of platinum. No tip more appropriate to the occasion could be imagined, as you had charged me with the duty of lighting the torch that is to be kept burning, in future, to illumine the memory of the man who, learning from Döbereiner, Edmund Davy and Wöhler, was the first to use, as a catalyst, the metal now valued so highly, which is an aid to man in so many ways and the most prized among metals by women. Indeed, platinum may well become the bond of union between the sexes, a bond that the fair ladies now in revolt may perchance hereafter admit, when the force of "some tonic" they "have drunk" is spent and the spell of Meredith's admonition is fully felt—

> Ah! madam, were they puppets who withstood
> Youth's cravings for adventure, to preserve
> The dedicated ways of womanhood?
> The light which leads us from the paths of rue,
> That light above us, never seen to swerve,
> Should be the home-lamp trimmed by you.

Mayhap, platinum, fit symbol of stability, will be used to light that lamp, for as gold has led woman to minister to man in the past, why not platinum in the future, especially as our gold is now reduced to paper which cannot be worn with effect as jewellery?

Saying this, however, I must not pass the chance to appraise the greatness of our art. Confided to a thionic embrace, even paper, in the chemic hands of the Courtauld firm, is now forced into the state of colloid and spun into a simulacrum of the butterfly's activity. The physicist but dreams of changing the atoms: we are facultative alchemists and transmute trees grown on the

cold heights of Scandinavia into stockings fit for the fair in the most heated climes. What can men of letters set against these achievements? On account of his works the chemist should be highly honoured of men in all the pathways of the world; woman has still to appreciate the part he plays in providing her not only with platinum and stockings but also with the complete series of rainbow tints which permit her to outrival not merely the peacock but even the lilies of the field: she little knows the extent to which in this and other ways she is his unconscious debtor. Still, the claim, nay the right of chemistry to rank as fundamental, not only to other sciences but to all human activity, has yet to be made clear; those historic lovers of ale, Wither, Pryn and Vicar, if with us to-day, could but agree that we have the right to think no small beer of ourselves. Is not this a point worth making on such an occasion, in this drab town which is so needful of beauty? Think what we could make of it, if we had our way; at least we could rid it of its chronic murky atmosphere, if not of its heritage of rickets.

To leave the serious, my task is to lay a foundation and set an example. Those who follow, with less opportunity to indulge in panegyric, will doubtless be moved to develop some special theme and carry Thionism to greater heights. Hence the propriety of my text,

Semper aliquid certi proponendum est,

which appears to have been Matthew Arnold's favourite maxim, as he cites it more frequently than any other in his *Note Books*. At least, it is a good one for a scientific essayist and Arnold is an honourable example to follow, as he was both critic and thoughtful, exact writer. The

chemist *should be* all these: is he, in any sufficient way? If not, why not? To take rank in the world he must not only hold his own against the best of his competitors but force his way ahead of them. To save the world from a Russian fate, science must be made as constructively effective in commanding human nature as it has been hitherto in hurrying the nations to their ultimate destruction. To-day, *you* are only thinking of speeding up the process of wasting Nature's resources and are giving little or no thought to their conservation. The chemist alone, through his thionic influence, has made the Northcliffe Press possible, the destruction of forests certain: think what that means! How will you counteract the evil work?

Our word-spinning literary friends—rather might we characterise them as enemies, so narrowly have they led the world, if we could think of them as other than thoughtless offenders—infer that we cannot express ourselves properly and Goths upbraid us from Cambridge that we are Greekless! Themselves, they have little regard for truth and realities, worshipping form rather than substance. It is difficult not to believe that they are consciously seeking to prevent us from coming to expression in the public service: how otherwise are we to account for the rare appearance in the Press of the scientific writer? He would be there, if in the least encouraged: is he perhaps feared and kept out, because it is felt that he might show up the futility of the hack writer or is it because journalism is now a close ring? Blame is often cast upon public taste but this is the herring across the trail: the public is not so simple as it is often made out to be and is willing to learn.

The man of words, in some degree conscious of their music, is more or less careful in their arrangement; he would not be paid for them if he did not place them with

fair effect. The scientific writer, who, be it noted, has usually had the same early schooling as the literary writer, has his attention so fully directed to realities and is so occupied in thinking out the consequences of his acts and in placing his work on record, that he is apt to give too little attention to style and rhythm. Too frequently therefore, he is verbose and lacking in lucidity; mere tricks of speech pass muster which should be avoided. To think every way at once is a little difficult, as those who have tried are aware. Yet not a few compare more than favourably with their literary colleagues—because they have something real to say. Darwin's *Origin* has often been cited as a model of clear statement: Huxley's studied style may be set against Ruskin's perfervid oratory: both were founded upon the Bible. Huxley's was not merely the product of genius but due to the exercise of thought and his sense of proportion, yet his utterances, at times, border on the sententious and if not less convincing, are certainly less alluring, than the sentimentalist's spontaneous ravings. Let us, however, be mindful of Milton's lines:—

> Thus they in mutual accusation spent
> The fruitless hours but neither self-condemning;
> And of their vain content appeared no end.

Each of us has sufficient task in clearing the motes from his own eyes: we should seek to work together.

Unfortunately, the pages of our chemical journals are full of examples of careless writing—of careless writing due to careless thinking. Little is done to overcome the influence of habit; self-criticism is rarely practised. We have no school of criticism to impose the needed discipline in our ranks. I well remember the effect on myself of a [*sic*] appended by that old Etonian warrior, Dr. Warre,

to a quotation he gave from a letter of mine, to which he was replying in *The Times*: though he could not field my argument, he caught me out over a split infinitive. Since then I have not repeated the heinous literary offence consciously and shall ever hold him in pious memory for his act of grace in curing me of the habit. It may comfort some if I say that I was once a dire offender. The current rumour that a free-lance journal may be established in connection with the Chemical Societies is an augury of a happier future—if only the pedantry of a publication committee of superior, elderly intolerants, without imagination, can be avoided. Free exchange of opinion, free criticism, is much needed among us; we are far too narrow in our outlook, too sensitive to remark; Professor Patterson's famous tilt over "But" is an amusing, extreme example of the intolerance of the hack editorial mind, worth remembering as an indication of the difficulties to be overcome and the danger we run in limiting freedom of expression.

> Is't not enough to make one strange
> That some men's fancies should n'er change
> But make all people do and say
> The same things still the self-same way?

Our position as chemists, the position of science, in the community, will depend far more upon words than upon works—upon the use we make of our English tongue. We must not only learn to weigh our words and use them effectively but use clean words, words that can be understood. Far from being Greekless, we are overfond of using an affected Attic terminology. Striking examples of ill-directed zeal are to be found in the pretentious manuals of so-called colloid chemistry. The bee in the bonnets of the dreamers in this field is the terminal *oid*. After wading through much colloid mire of late, I am

wondering whether the 15,000 odd members of Dr. Parson's happy and obedient flock of chemists in the land of Wilder D. Bancroft do not consider suspenders a vulgar term for braces and wear their pants adsorbed by suspendoids. If I be not misinformed, the younger ladies now wear corsoids and chemiseoids, no longer the real thing; in fact, I believe all feminine garments are *oids* in these days, except hose, perhaps—and this because chemists have made them of an attractive *sericoid* material. Everything seems to be now a shortened, sort-of-a-kind-of what it used to be; canned goods have captured the world and impudent advertisement counteracts conscience.

I trust what has been said will suffice to

> Force you by right ratiocination
> To leave your vitilitigation
> And make you keep to the question close
> And argue dialecticos.

The need of care has been specially impressed upon us, of late, owing to the attitude adopted by the Official Referee of the Board of Trade appointed under the Safeguarding of Industries Act, 1921. Nothing could be more humiliating than the manner in which, sitting as a Delphic Oracle in Whitehall or the Law Courts, this gentleman has created chaos in Chemistry by his pronouncements upon our vocabulary. The discussions on the subject in various Sections of this Society have been far from illuminating; the lack of agreement among speakers, in fact, is sufficient proof that clear thinking is not yet our characteristic.

Mr. Edmund Gosse tells us, on the authority of the Marquis de Racan, that the leader of the classical reaction in France, M. de Malherbe, one hour before he died, woke with a start out of a deep slumber to rebuke his hostess,

who was also his nurse, for using an expression which he did not consider to be correct French. When his confessor ventured to chide him, he replied that he could not help it and that he wished to preserve up to the moment of his death the purity of the French language.

My exhortation is, in like manner, that we should be content only to play upon

> . . . the lyre of language clear
> Love's tongue and source,

one of the most perfect of Meredithian couplets.

To return to platinum, to mention it is to excite the imagination in many ways. Its attributes are of such perfection that the metal must have been Nature's first care had due forethought been exercised at the Creation: it is clear that little as there is now, in the beginning there was no conscious science, otherwise platinum would be as iron in quantity and much more oxygen free in the world. The electrons, however, seem to have been self-willed and proportions may well have been determined merely by their affinities as influenced by transcendental temperatures, just as is the complexity of benzenoid hydrocarbons at ordinary heats.

Iron has many attractive qualities: without it perhaps the world would have been colourless and drear; without it perhaps we could not have been fed with air; yet it has many imperfections:

> Ah me, what perils do environ
> The man that meddles with cold iron.

Never were we so mindful as now of its misuse and we are striving to minimise this to the utmost but as usual

are lacking in outlook, leaving chemistry out of account and failing to take proper measure of human nature and its structural stability, failing to realise that the problem is chemical at bottom, living Nature being but one huge laboratory, in which structure is the main determinant of function, its operations largely catalytic.

If platinum could be used as iron much trouble and loss would be avoided: polish and paint would be far less in request; of no knight's pistol could the mock-heroic have been written—

> But Pallas came in shape of rust
> And 'twixt the spring and hammer thrust
> Her gorgon-shield, which made the cock
> Stand stiff, as if 'twere turn'd t' a stock.

Think of the chemist's generations-old struggle to decipher the mysteries of rust: what it will eventually be worth to us if all iron be made rustless!

Helmholtz's complaint against Nature of the imperfectness of the eye is a small matter in comparison with the lament the chemist may utter as to the scarcity of platinum: the uses to which he could put it are so many and so important. The man whose mentality it is my allotted task to picture, a task of exceeding difficulty, was the first to give it to full industrial use: this was his great achievement.

We often spoke of its wonderful activity; I more than once said to him, "When you have done with using it, we will set to work together to find out, if possible, how it does its work." That day never came and seemingly we drifted away from our purpose: he stuck to sulphuric acid and kept his platinum in technical use; whilst occasionally taking a sip at the acid I began to play with organic catalysts, not uninfluenced by the thought of his disease; there was no money in them but they gave what

I believe to be the final clue to the behaviour of platinum. I little thought that I should be called upon and privileged to display my knowledge in his honour.

RUDOLPH MESSEL

I first met him in my initial year of office as a Secretary of the Chemical Society, in April, 1876, on the evening when Dr. Squire and he described and demonstrated the process they had developed of manufacturing sulphuric anhydride, already in operation at Silvertown. He was elected a Fellow of the Chemical Society that same evening. I was the only speaker to break the harmony of the meeting by suggesting that Nordhausen sulphuric acid was not a mere solution of the anhydride but mainly a definite acid, a compound of the anhydride with sulphuric acid, anhydrosulphuric acid, then unrecognised except by Schützenberger. I trod on Messel's heels with a paper on "Systematic Nomenclature": this, too, shadows me to-day.

I was greatly attracted to him from the beginning and we soon became fast, I may say, affectionate, friends. Perhaps I surprised him by knowing the work he had done as a student on strychnine and maleic acid: I would here emphasise the fact that he started his career as a chemist on the organic side. Moreover, I had been ahead of him in cultivating the acquaintance of sulphuric anhydride—on German soil—as it was the subject of my Ph.D. thesis, published in English in the *Proceedings of the Royal Society*, under Frankland's patronage, in May, 1870, under the modest title "Contributions to the history of the acids of the sulphur series. I. On the action of Sulphuric Anhydride on several chlorine and sulphur compounds." This was my introduction to the Royal Society. A little

later, in 1871, I made my first appearance, as an independent worker, at the Chemical Society, with a paper on the use of sulphuric chlorhydrol as a sulphonating agent. Messel was afterwards led to take an interest in this compound through preparing it for me.

I thus came under thionic fascination at an early stage of my career and was fully prepared to appreciate Messel's work and its value, the more as I had worked alongside Graebe in Leipzig and Perkin was my fellow secretary.

Messel was born January 14, 1847, in Darmstadt. He died April 18, 1920, at his chambers in Victoria Street, London. He was of Jewish extraction but professedly Lutheran.

To-day I will give only a brief survey of his history, sufficient to make clear his proclivities and the influences to which he was subject.

His father, Simon Messel, was not originally intended as his father's successor in the banking business but was apprenticed to a Parisian maker of artistic furniture, which accorded more with his own taste for art. The interest of this fact lies in the indication of the source of the highly developed artistic tastes which most of his children evinced. Before he had completed his training in Paris, however, Simon Messel was recalled to Darmstadt to take the place assigned to his elder brother, who had journeyed to America and there disappeared from the sight of his relatives. In consequence of this change, Rudolph Messel's early years were spent in what for those days ranked as affluence and his father was able to provide adequately for his education. He was the second of five children, of whom four were to make their homes in England; the fifth acquired great distinction as an architect in Berlin.

He received his elementary training at Schmidtz's Academy in his native city. Shortly after his father's death in 1859, he was sent to a Huguenot school at Friedrichsdorf in the Taunus, where he remained until early in 1863, that is to say, until he was fifteen years old. His early interest in science and his precocity are shown by the following reference he made to this period in his Presidential Address to this Society in New York in 1912.

"In 1861, when I was at school at Friedrichsdorf, in Germany, my master, Philip Reis, invented the first telephone. I was present at its birth and assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit, speaking or singing, I listening at the other or *vice versa*."

While he was at school, the family circumstances had changed and it was clear that Messel would have to support himself at an early date. His intention, formed during the last years at school, was to become an engineer, either civil or mechanical. In January, 1863, he discussed his future course of action with an old friend of his father's, Heribert Rau, an author of some distinction, then living in Frankfort. Rau wrote to him a letter strongly advising against this choice of a profession, basing himself upon the fact that the demand for engineers already fell short of the supply, whilst the boy's religion would, he said, militate against his receiving a State appointment. If the boy were father to the man, as all accounts indicated that he was, Rau knew well the love of independence and self-reliance which were among his young friend's salient characteristics. After citing the reasons given above, he lays the greatest stress upon the fact that to become an engineer would entail many years of study preceded by years of practical work at the bench, so that

the day when he would be able to support himself must be far distant. He then gives the young Rudolph positive advice, which it is clear determined all his future. He bids him devote himself to the study of commerce, which, he said, would rapidly lead to independence—and to combine with this the study of Chemistry, Physics and Technology and so become a manufacturer. Rau seems to have felt that to become a manufacturer was a great falling away from grace for an ardent boy, because he goes at great length into the great future which lies before him and the noble examples of enlightened and well-spent lives which were to be found among the great manufacturers of the day. Finally, he advises Messel to move to Frankfort, to enter the business of some large merchant, to attend at the same time lectures in Chemistry, Physics and Technology and after completing his apprenticeship, to travel to France, Belgium and England, the lands of factories and industry, to keep his eyes open for this or that article the making of which was urgently needed and to become himself a factory owner.

That Messel's whole course of action was influenced by this letter is clear, not only from the fact that he kept it to the last amongst his rarest treasures but that he followed the advice it contained, almost verbally.

In April, 1863, he became apprenticed to E. Lucius, in his wholesale drug, chemical and pharmaceutical factory in Frankfort, where, according to a letter from Lucius, be obtained a thorough knowledge of the business in all its branches. He remained in Frankfort until September, 1866. Although there is no definite evidence that he attended lectures at the same time or who his teachers were, there can be little doubt that in this respect also he followed the advice given him. In 1864 and 1865 he was a member of the " Physikalischer Verein," which was then and later a teaching institution; the teacher in

chemistry was Prof. Rudolph Boettger and in Physics first Prof. Oppel and later Prof. Friedrich Kohlrausch.

On leaving Lucius, Messel entered the Federal Polytechnic in Zürich, where he followed the regular first-year course. Among the subjects taken were organic and inorganic chemistry (taught by Städeler); technical experimental physics (taught by Bolley); mechanics, mineralogy, botany and technical drawing. Messel completed his year in Zürich. The following winter he spent at Heidelberg studying organic chemistry under Erlenmeyer. According to a letter from Bunsen, he worked too with the utmost zeal on analytical subjects in the laboratory of that great teacher, then in his prime. Bunsen, who wrote two years later, especially mentions Messel's manual dexterity, which he says was clearly shown in his later published researches on strychnine-oxyethylene compounds and sulphomaleic acid.

From Heidelberg Messel moved in the spring of 1868 to Tübingen, where he finished his education. Here he spent a year attending the course of experimental physics of Prof. Reusch and courses in organic, inorganic and analytical chemistry by Prof. Strecker. From the spring of 1869 onward he appears to have been engaged in various inquiries under Strecker. A description of those referred to by Bunsen in the letter noted above formed the thesis he presented for his degree. Messel left Tübingen for England in April, 1870.

I believe he came to England originally to act as private assistant to Roscoe. During the short period he spent in Manchester, he worked both with Roscoe and Grace Calvert. The outbreak of the Franco-Prussian war, however, led to his recall to Germany. Owing to some physical defect, he did not serve in the army but was relegated to the Ambulance Corps; he was wounded while on service. When recovered, he returned to England,

where he remained during the rest of his life and ultimately became an Englishman. He entered the service of Dunn, Squire and Co., at Stratford, as assistant to Dr. Squire and here he became a thionist; but the virus was already in his veins.

In his Presidential Address, he tells of a conversation in the beginning of the 70's with his former teacher Strecker, of Tübingen—who was the first to discover the relationship of alizarin with anthracene—and Brüning of Höchst, on the importance of fuming sulphuric acid in the synthetic alizarin industry, then rising into importance. To his question, how the acid should best be made, Strecker gave the prescient reply: "That is a problem for you to solve." A few experiments convinced him, he says, that given pure gases, the catalytic action of platinum was the rational solution of the problem. On April 8, 1875, a telegram came to him at the laboratory, from Squire, asking him to read up that night about Nordhausen acid, as it was wanted by an alizarin works. The response was Messelian and immediate: no reading was necessary. Next day he showed how simple a matter it was to marry sulphur dioxide with oxygen by means of platinum. However, Squire was conventional and thought that the decomposition of an acid sulphate would be a simpler method. Experiments were made as requested but eventually Messel was told "to try his dodge."

With Messel to try what he had once conceived as practicable was to succeed. He was there already; he had seen and he conquered forthwith. A patent was taken out by Squire in 1875 and the process was described at the Chemical Society early in 1876. Meanwhile, Squire had established as a new firm Squire, Chapman and Co., with Messel as factotum; he would have objected to my calling him chemical-engineer, as he had no belief

in half-breeds, also he was an entire disbeliever in the attempt to bring the works into the laboratory.

The process was established at Silvertown and in 1878 he succeeded Squire as manager of the works, which he only quitted in 1915, when his health gave way under the excessive strain of the times.

The paper Messel and Squire read at the Chemical Society was never published: even I cannot say why; probably because of patents; from a remark made by Messel, I gather that it was not sent in by Squire. The record of the meeting on April 20 in the *Chemical News* runs simply as follows:

"The speaker (Messel), after giving a sketch of the history of the manufacture of sulphuric acid, described the process for preparing the anhydride. The vapour of ordinary sulphuric acid is passed through a white-hot platinum tube, whereby it is almost completely decomposed into water, oxygen and sulphurous anhydride: the mixed gases, after passing through a leaden worm to condense the greater portion of the water, are completely dehydrated in a leaden tower filled with coke, over which a stream of concentrated sulphuric acid is allowed to trickle. The dry mixture of oxygen and sulphurous anhydride is now passed through platinum tubes heated to low redness and containing fragments of platinum pumice, when the gases recombine to form sulphuric anhydride which is condensed in a series of Woulffe's bottles."

In early days, I was a frequent visitor at Silvertown, where Messel not only worked but also lived in the modest quarters of a small house attached to the works, uutil he removed to chambers in Ebury Street and afterwards to Victoria Street. Characteristic of the man throughout his career was his unpretentious, simple mode

of life. I only knew him to be vain in one connection—as President of this Society; but he was very proud of the F.R.S. and not a few of us were proud of him as a colleague. Generous and ever thoughtful of others, unselfish to a degree, he had little thought for himself and a hatred of all display; the artist came out, first in his extreme devotion to his own art—for chemistry, technical chemistry in particular, is an art—then in his love of the company of artists and other bohemians: he was a great admirer and friend of Gilbert—of Gilbert and Sullivan fame—and a constant frequenter of the Savage Club; may I add, as a judge of quality in Champagne; in Weib and Gesang he had no estate, though he was musical. Living among them, he knew his work-people and was in sympathy with them: hence his popularity and power.

One understood his success when one followed his work. A man of astounding vigour and full of feeling, he burnt the candle at both ends and all over its surface. That he lasted so long always surprised me. When about sixty he was overtaken by diabetes. He was everything—not only chemist, engineer and business man; he also took care to cultivate the social side of his life; he was the only manufacturer of my acquaintance who attended regularly at scientific gatherings and showed real interest in the proceedings. He was thorough in everything he did. Probably he did far too much himself but he could not suffer fools gladly, though not often impatient outwardly and always considerate. He had no hobby outside his business and science. During many years, his one way of recuperating was a weekly visit to Brighton on Sundays. He went down by the early train, walked out to the Devil's Dyke, had lunch and then returned to town, usually to spend the evening with friends. In those days he was a real walker, as I found when occasionally his joyful companion.

Those who knew him, especially in the early days, will remember his vigorous frame, his black hair and sparkling eyes, his smiling face, his hearty bass staccato laugh, his peculiar guttural accent. If his portrait were to be painted, I think we should ask the artist to depict just that smile alone, following Tenniel's living presentation of the Cheshire Cat up in the tree by its grin. We can fancy him to-day, smiling at King Ruttan and his crowd and at me the executioner, chuckling at my use of the axe of criticism. He never mastered English properly, though he spoke it fluently. He was very fond of young people, many of whom rejoiced in his generosity. We who knew him all think of him as one of the most lovable men we have met. His outlook on life was always cheerful and optimistic but he was a close observer and critic; always broad, clear and careful in his judgments but deliberate in forming them. The example he set in leaving his fortune to science is a remarkable one and best proof of his considerate outlook. Honest and sincere himself, he hated insincerity and all meanness of spirit. He combined in his person all the best of German good qualities, fired and softened by Jewish imagination.

Nordhausen or Fuming Oil of Vitriol was the only kind of sulphuric acid known to the early chemists. Even in comparatively recent times, not more than a hundred years ago, the manufacture of vitriolic acid, by burning sulphur, was so imperfect a process, that the old method, troublesome and crude as it was, still held its ground.

The production of the anhydride, by decomposition of a sulphate, appears to have been known in very early times, indeed up to the year 1736 the only way of preparing sulphuric acid was to evolve vapours of the anhydride

by destructive distillation of a sulphate and to pass these into water.

When Messel and Squire began their work, Baron Stark, in Bohemia, was sole maker of the fuming acid, the process he used being substantially that of Basil Valentine, born 1394. A particular kind of Pyrite was weathered (oxidised) by exposure to the air. The copperas (ferrous sulphate) so formed was dissolved out and the solution concentrated. The sulphate crystals which separated were usually sold; the mother liquor, containing much ferric sulphate, was then evaporated to dryness and the residue slightly roasted, so as to dry it. The vitriol-stone, as it was called, so produced, was broken up and charged into small bottle-shaped retorts arranged in a gallery furnace, in such a way that they could be heated to a high temperature. Instead of receiving the vapours in water, as in making sulphuric acid, they were condensed in oil of vitriol, a small vessel containing the acid being luted to each retort. The distillation lasted about 36 hours and as the quantity put into each retort was small, the product was also small. The consumption of fuel was great and much labour was involved in charging and discharging the retorts, many of which were broken. The process required great skill on the part of the workers. All attempts to manufacture the acid in larger apparatus appear to have ended in failure.

At the outset, when the attempt was made to produce the anhydride by passing the vapour of burning sulphur mixed with air over heated pumice coated with spongy platinum, the chief difficulty met with was in condensing the anhydride. As Messel and Squire remark—the manner in which sulphuric anhydride will evade condensation from a gaseous mixture is something quite marvellous. When pure gases were used, the condensation

was easily effected; on this account, in the early days, of the industry, when the value of the fuming acid was much greater than that of oil of vitriol, a suitable mixture of sulphur dioxide with oxygen was obtained by decomposing the latter acid. In their experiments referred to in the paper, a small platinum still about 4 inches in diameter was so arranged in a Hofmann Gas Furnace that it could conveniently be maintained very nearly at a white heat. Ordinary oil of vitriol was slowly fed into the still and kept strongly boiling; the vapour was almost completely decomposed, the condensed water containing but little acid. After the mixture of gases had been dried by means of sulphuric acid, it was passed over pumice stone prepared with platinum, enclosed in a large tube made of thick platinum foil, which was heated to a dull-red heat by the waste heat of the gas furnace. Little or no sulphur dioxide passed away when the heat was properly managed, the process was continuous and the condensation perfect. Nearly 70 parts of anhydride were obtained from 100 parts of white sulphuric acid, the theoretical amount being 80 or thereabout.

In the early days, the demand was limited by the requirements of the dyestuff industry, especially that of the madder colours. When the use of the fuming acid was introduced into the Cordite industry, in connection with the displacement nitration process, the demand became much greater. At the close of his industrial career, Messel was producing from 250 to 300 tons of Oleum per week, containing 20% of anhydride, in admixture with sulphuric acid.

As experience was gained and the difficulty of condensing the anhydride was overcome, sulphur dioxide prepared by burning sulphur and ordinary air were used. In this case also exact proportions were at first adhered to. I remember Messel telling me that he was first led

to use excess of air and therefore to abandon the use of special appliances for the supply of the gases in due proportion by having his attention called, by his workman foreman, to the fact that the plant worked better when air was supplied in excess.

In early days, to reduce the cost of carriage, acid was sent abroad of 80% anhydride strength and diluted with "monohydrate." Where this was done I forget but that this was his practice I know, as when I once asked him if he had any knowledge of the process of making sulphuric acid (H_2SO_4) by freezing it out from oil of vitriol, he told me that he had at one time so made it for the purpose stated above.

Over and over again he told me that he aimed at making vitriolic acid by his process as cheaply as by the chamber process and I well remember the joy with which he told me that he had at last succeeded.

Messel's claim to distinction does not rest upon the discovery of a chemical process but upon his initial success in building up from the foundation, unaided and almost alone, a novel industry of great importance and in having solved a variety of technical problems of extreme difficulty. His success was due not only to his great mechanical ability and clear understanding of the task before him but particularly to his high moral standard and his absolute devotion to work.

> The strongest weapon one can see
> In mortal hands is Constancy.

Doubtless, in later days, as we all do, he derived assistance from outside but this was only when his primary work was accomplished and it became necessary largely to extend the plant. We have been accustomed to admire the systematic manner in which the German chemical works are conducted with the aid of a

considerable staff of trained, disciplined workers: what always appealed to me was the fact that he, a German working under our English conditions, with scarcely any technical staff, was long far in advance of his countrymen. His success was due, in the first place, to his thorough scientific training and to his scientific outlook but, to an exceptional degree, to his moral attitude towards his work. The lesson to be learnt from his life should be of no small value to us.

CHEMICAL ACTION *AND* CATALYSIS

AN ESSAY ON CLEANNESS

"*A Satyrical Allusion to the Heathen Gods, who are supposed all of them to have been Kings or famous Men in their Time and fabl'd into Deities by the Error and Ignorance of those Days; concluding with a list of Great but Vicious Princes in our Modern Times fit to make Gods of in the next Promotion.*"

Chemical Action *and* Catalysis: if not these words, καταλύω should be graven at the base of the monument to my friend.

The industry which Rudolph Messel had so large a share in developing, more than any other perhaps, is commonly thought of as one in which "*catalysis*" has a leading part: every budding student during generations past has been taught to regard nitric oxide as the catalytic agent in the *chamber process* and platinum as similarly effective in the later *contact process*. No two less similar processes could well be imagined; yet if choice were to be made between them, I imagine the latter would be regarded as the "typically" catalytic process.

Berzelius, in first communicating his conception in 1835, included a long list of interactions under the influence of agents which appeared to take no permanent part, even if included in the change, as they were ultimately recovered unaltered.

Whilst in the interval attention has been more and more concentrated upon platinum, nickel and the enzymes as catalytic agents *pur sang*, of late years there has been a growing tendency to extend the conception to all agents determining change—in other words, to chemical change in general.

A strange confusion of thought prevails, in fact: rather, may it be said, perhaps, a strange lack of thought. Francis Bacon three hundred years ago could point out, that "the ill and unfit choice of words wonderfully obstructs the understanding." The term catalysis would seem to be one of those "Idols of the Theatre," as he terms them, "which have immigrated into men's minds from the various dogmas of philosophies and also from wrong laws of demonstration."

If, as Bacon insisted, "words force and overrule the understanding and throw all into confusion and lead men away into numberless empty controversies and idle fancies," it behoves us to be most careful in our choice of words and concise in our definitions, remembering that "even definitions cannot cure this evil in dealing with natural and material things, since the definitions themselves consist of words and those words beget others, so that it is necessary to recur to individual instances and those in due series and order."

It is a strange fact that whilst the "criteria of catalysis" are more or less fully discussed in recent works, there is practically no reference to the broader problem of chemical change or action; even Mellor, in his two encyclopædic volumes, makes no attempt to consider the

conditions which determine it. This is equally true of the lengthy dissertation compiled by the pillar of American Physical Chemistry, Wilder D. Bancroft and his adsorbed body of assistants. The recent discussion at the Faraday Society, apart from Langmuir's experimental contribution, appears to have been in a "greenery-yallery, Grosvenor-Gallery" Valhalla to which chemists can never hope to attain—only Dr. Lowry spoke from a foundation of fact, in earthly but shattering terms.* The main lesson to be drawn from the two documents is that Dr. Miall should continue his efforts (of which he has given notice in the U.S.A.) to found an Association for the Discouragement of the Integral Calculus.

Students, we know, have been taught of late years to worship Idols of the Theatre, to lisp certain Teutonic shibboleths; but the inner mysteries of chemical change have never been confided to them. The state of ignorance

* Bancroft's essay is written with child-like innocency of purpose. He meanders through three numbers of the *Journal of Industrial and Engineering Chemistry* (April to June) without ever stating what he thinks he means by catalysis, without making the slightest attempt to overlook the process of chemical change in general. Like most chemists of the time, he seems to be clad in little more than a chemical loin [? l'ion] cloth: that a whole suit is necessary for a change seems never to have occurred to him. Such be your gods, Oh Israel!

The same sense of disappointment is left on turning over the pages of the monographs on the subject. Jumble sales of facts, vastly interesting and valuable as catalogues of observations, they lead nowhere in particular:

> When they cry, "Steer to starboard but keep her head larboard,"
> What on earth is the Helmsman to do?

The mind is reduced to the condition of the map so vividly described by the Bellman in *The Hunting of the Snark*—"A perfect and absolute blank."

The statement made by Samuel Butler, under the heading "First Principles," is worthy of quotation in this connection:

> "When we are impressed by a few only or perhaps only one of a number of ideas which are bonded pleasantly together, there is hope; when we see a good many, there is expectation; when we have had so many presented to us that we have expected confidently and the remaining ideas have not turned up, there is disappointment. So the sailor says in the play: 'Here are my arms, here is my manly bosom but where's my Mary?'"

Indeed, "Where's my Mary?" must be the general cry of those who read of catalysis in the journals; we miss her dear form everywhere.

induced by our text-books is astounding: a vast burden of facts is laid upon us but processes are rarely considered: the manuals mark no advance in methodical treatment and are best described in Shelley's words as:

> . . . tomes
> Of reasoned wrong, glozed on by ignorance.

We physicians have a long way to go in healing ourselves before we prate of scientific method to the public. As to text-books, let us Scrap the lot! *

> *Spermatick Vigour* spreads the poison'd Race,
> Conveys Hereditary Crimes apace;
>
> . . . . .
>
> What strange, what inconsistent Thing's a Man?
>
> . . . . .
>
> Who shall his Nature search, his life explain?
> A constant Bondage bows his Couchant Neck
> His Will corrupted and his Judgment weak.
>
> . . . . .
>
> Subjected Man submits to the Controul
> Of Forty Thousand Tyrants in his Soul.
>
> . . . . .
>
> *Wonder no more* the Sons of such a Race
> Grow ripe for Slavish Principles apace;
> The Victory of Vice is so Compleat
> The Conquer'd Faculties at once submit:
> He's born with Slavery in his very Face
> And hands it down to his subjected Race.

* It is estimated that new books will be "Homeless" at the Chemical Society five years hence. It is clear that a "Palace" must be found in which the united Chemical Societies can foregather with the books of the future and those of the past which are worth preserving; no other Catalyst will serve the purpose. Meanwhile let selection be made of the few text-books worth preserving and let the rest be publicly burnt, as a warning to budding authors: there will then be sufficient room on the shelves to meet passing needs while the Palace is building.

In R. L. Stevenson's apposite words: "Culture is not measured by the greatness of the field which is covered but by the nicety with which we can perceive relations in that field, whether great or small."

Thus defined, where is the cultured chemist to be found to-day? Recent hearings before the Board of Trade Official Referee show that the witnesses—I will not call them chemists—were not even agreed as to what is "A Chemical"; the innocent lawyer was trapped into the belief that it was something manufactured.* Doubtless this definition was paid for—nothing else could explain and excuse its absurdity.

Chemical Change

All single things dealt with by the chemist are chemicals. A chemical can only be defined as a material which can take part in a chemical change; combustion undeniably involves chemical change: argle—Oxygen is a Chemical! Who manufactured oxygen? We can only say—It is!

What is involved in the process of Combustion—to take the simplest possible case, that of the formation of *hydrone* (water) from hydrogen and oxygen? Every text-book we have *lies* in telling the student that hydrogen and oxygen interact to form "water." We *know* they do not. The effect of drought upon the country is patent to everyone—especially of late years—yet no notice is taken of its effect in chemistry. The remarkable work of Wanklyn, Cowper, Dixon and especially of H. B. Baker may be just mentioned occasionally but its entirely

* Judgment upon the Act was pronounced by the author of *Robinson Crusoe* when he said:

> "Reason is the Test of the Law; for Laws which are contradictory to Reason are void in their own Nature; and ought not either to be made or regarded."

fundamental value is in no way appreciated; Lowry's work may be seen but it is not heard.

It is as Bacon said three hundred years ago: "The Idols and false notions which are now in possession of the human understanding and have taken deep root therein not only so beset men's minds that truth can hardly find entrance but, even after entrance obtained, they will again in the very instauration of the sciences meet and trouble us, unless men, being forewarned of the danger, fortify themselves as far as may be against their assaults."

Surely it were time that we fortified ourselves; that we sought to deserve the title of scientific workers and thinkers? Human understanding *is* frail and limited but not so limited as we make it appear. There is no conscious effort made by us to be impartial and logical and our difficulties arise from lack of culture—from the gross specialisation of the day, which is largely conditioned by our satanic system of competitive examinations: a system more calculated to kill genius and prevent progress could not possibly be devised.

Yet hope is in the offing. To me it seems, I am glad to say, that, in upper scientific circles, there are clear signs of a return to chemistry and reason—that the attention paid to pseudo-physical aspects having outworn its welcome is giving place to the desire to consider the inner meaning of chemical phenomena, to be eclectic, to recognise the insufficiency, if not the emptiness, of the treatment to which they have been subjected by the Syncretists. The work done by Hardy in correlating lubricating power with chemical structure and that of Jacques Loeb, following that of Hardy, on proteins, may be referred to by way of example. We are returning to the sane vision before the early workers that molecular structure is the key to function; let us hope that the

change will be marked by the rejection of the pedantic jargon which has so long marred the fair field of our science.

From morning to night we must impress upon our students that they must learn to think for themselves but that thinking rightly is an outcome of experience, no easy thing: that they must therefore give due heed to experience but have no belief in authority—above all, be wary of the journalist and propagandist and of the text-book.

The experimental evidence put forward by H. B. Baker is of such cogency that it may now be asserted, that hydrogen and oxygen *cannot interact* and that to determine interaction *a third component must be introduced into the system.* What is the nature of the third component? Whilst affording proof that moisture promotes the change, Baker's observation that liquid water might be present and yet no explosion take place, apparently, is proof that water alone cannot act as third component. By using the hardest glass and gases liberated from a solution of baryta, Baker eliminated acid impurity as far as was practicable; as interaction takes place when these precautions are not observed the legitimate inference is that water becomes the determinant only when it is rendered conducting by the presence of impurity, usually acid. The interaction is an electrolytic process, in fact. Faraday taught this doctrine, in early days (1833). By his study of the power of metals and other solids to induce the combination of gaseous bodies and of electro-chemical decomposition in general, he laid the foundation, for all time, of the theory of chemical change; nevertheless, whilst honouring it in its transcendental aspects—for we recognise that Faraday foreshadowed the electron—we pay no attention to the ordinary applications of his work. Why is it that we so rarely read in

order that we may mark, learn and inwardly digest? Whatever of logic I have in my composition, whatever unfortunate tendency to be critical, I owe it, in some measure, to Trench's *Study of Words* but mainly to reading Faraday. An early purchase of his collected works was the most fortunate I ever made. The exquisite lucidity of his logic at once impressed me. The Electro-chemical Researches are in *Everyman's Library* and every youthful student who wishes to gain the scientific habit of mind should acquire and master this volume—if only as a literary exercise. All the essayists may well be put aside for it, if the desire be to cultivate style and to escape from the tyranny of the literary plagiarists who eternally harp upon one theme and make no attempt at progress.

To-day, I but take up the position I took with reference to Baker's work in March, 1885, when he was only beginning his chemical studies—merely telling us that the combustibility of phosphorus and charcoal had been overrated and misinterpreted. Influenced by a Faradic current of thought, intensified by my association with two pioneer workers in electricity, Ayrton and Perry, I dared to project my mind into the future and say that some day it would be found that a mixture of pure hydrogen with pure oxygen would be inexplosive. The position, I assumed, was perfectly simple—that action always takes place and only takes place in a conducting or electrolytic circuit. Neither gas was a conductor nor did either make water conducting. Following Ayrton and Perry, I argued that Ohm's well-known electrolytic law, C = E/R, was equally the law of chemical change. My forecast was verified by Baker in 1902 and he has since given not a few other proofs of the validity of my thesis.*

* As the Proceedings of the Chemical Society are not generally available, I venture to reproduce my prophecy :

"He (Dr. Armstrong) had even ventured to affirm to Mr. Dixon that

I venture to think that the discussion we had on th occasion referred to at the Chemical Society is the mos important in its history and yet how little real recognitiō it has received. Who reads such literature, any re: literature, to-day.* The Tit-bits miscalled abstracts an illiterate text-books alone hold the field. Very few remai mindful of Liebig's counsel to Kekulé: "No one wh does not ruin his health with study (he meant reading will ever do anything in chemistry nowadays." Som excuse, perhaps, is to be found in the quality of to many modern memoirs.

Altars have been set up everywhere for the worship c a narrow doctrine mislabelled Physical Chemistry; th chief Ikon has been St. Arrhenius, a divinity of Scandi navian origin; Teutonic priests, the Ostwalds especiall have ministered faithfully at his shrine; latterly the have gradually changed the material of his effigy and hav formed it in glue. The fashion set has not only stuck i many places but has assumed epidemic proportions. Th ritual the school has developed is as vague, as wordy an

some day it would be ascertained that a mixture of pure oxygen wit pure hydrogen was not explosive.

"Dr. Armstrong said that the view which he now held was best state by defining chemical action as *reversed electrolysis*, *i.e.*, in any case i which chemical action was to take place it was essential that the syster operated upon should contain a material of the nature of an electrolyt Neither oxygen nor hydrogen was an electrolyte, therefore a mixture c only these two gases should not be explosive; a mixture of pure oxyge and pure carbonic oxide for like reasons should not explode. There wa however, a tendency perhaps to exaggerate the importance of water an to overlook the possible presence in minute quantity and influence c other bodies. Water not being an electrolyte, as it was scarcely probabl that water and oxygen or hydrogen would form an electrolyte, it wa difficult to understand that the presence of water pure and simple shoul be of influence in the case of a mixture of oxygen and hydrogen."

* The Americans, almost more than the French and Germans, now pa scant attention to outside literature and are on the way to give a new meanin to the term Monograph—not the graph of a subject but that of a notion Falk disregards the whole of my work, including that on enzymes, in hi monographs.

as mystical as that of any of the Churches. Leipzig for a time was a veritable Lourdes and full of pilgrims; everyone knows the miraculous cures that were issued from the temple there. The prominent symptoms of the disease is that it renders the mind semi-permeable to ideas; if any, only those of one kind get through. However, we all have partially permeable intellects—not semi only but some much smaller fraction. The Americans, as was to be expected, have been worst hit; we come next; the French have displayed their characteristic immunity towards external influences and have shown a sense of proportion which has enabled them to preserve their sanity. No cult can last for ever; some free men there still are in the world; the war has made people think a little; shortly we shall realise how silly we have been in adopting clerical methods and substituting faith for evidence, particularly in putting faith in any one hypnotist and allowing him and his lieutenants to dogmatise us into belief. Science is a human occupation like others; we are all prone to hero-worship and seekers after praise and position, making pleasurable statements, are always taken too much at their own valuation; when followed by the trail of Nobelism they are irresistible.

There is nothing dogmatic in the assertion that all chemical change is an electro-chemical, *i.e.*, an electrolytic process—facts prove it to be such: let those who doubt study Faraday. Modern discovery only serves to deepen the conviction. The nature of the electro-chemical process, however, is still open to argument.

To the pure all things are pure, it is said. Still, none of us dare claim to be otherwise than impure and so we may reverse the proverb and say that to us, the impure, all things are impure. Strange to say, the physicist is still affecting to love the simple life and has not yet learnt

to take things impurely: he has yet to recognise the value of chemical soap-and-water, the need of attaching importance to cleanliness, perhaps it should rather be said, to dirt; his interpretation of the phenomena of electric discharge has yet to be justified under dry conditions. The intermediary is difficult to find. Langmuir seems to be the most likely holder of the office, if he can but come down to earth and be proportionate in his judgments—in Faraday's sense; if he will work at the open window.

The Determinant

Most will now admit that the interaction of hydrogen and oxygen is *determined*—please mark the word—by conducting water. What is conducting water? The Arrhenists claim that water itself is a conductor—though only a very feeble one at best. I need not remind that the plea, "It's only a wee one," is not admitted in law. The assumption that water is a conductor *per se* is purely gratuitous. The value accepted is that arrived at by Kohlrausch—but he worked in prehistoric times and used prehistoric methods; he cannot conceivably have dealt with pure water. Pure water is impossible in mortal hands. Some minute impurity must ever be present. Knowing as we do that impurity is present and that conductivity falls rapidly as impurity is removed, it is only logical to assume that ideal, pure water would be a non-conductor, at least to all ordinary potentials. The situation is one which cannot well be resolved by experiment. We must proceed by way of hypothesis, as in the case of gravitation.

Let our hypothesis be this—that the interaction of two diverse molecular systems is determined by the presence of a third system, itself an electrolytic system and compatible with them, in the sense that the three

can be associated into a single conducting system. I would call this third system the *Determinant* and say that every chemical change involves the presence of a Determinant. Please mark the word *Determinant* and note that the Determinant is always an electrolyte.

Sauce for the goose being sauce for the gander, all that I have said may be read backwards. If hydrone cannot be formed by the direct interaction of hydrogen and oxygen, it cannot be directly resolved into these; some determinant must intervene to bring about the decomposition. H. B. Baker has given proof of this thesis by showing, to take only a single case, that the stability of ammonium chloride is greater the more carefully it is dried.

Recognising this, let us give effect to our belated conversion to a true faith by including in every equation the symbol of the determinant, E or Ed, a small one, if you will; better an epsilon, ε, if not $\varepsilon\delta$, as these foreign signs will have greater appearance of learning. Let us not be ashamed of acknowledging the determinant, especially in Grecian dress, as a necessary member of any family party of chemical agents we may call together, *e.g.*, in expressing the formation of hydrone empirically, in order to show what factors are involved, let us write:

$$(O_2 + \varepsilon\delta + 2H_2) = 2H_2O + \varepsilon\delta;$$

or if we wish to represent the operation as a reversible change

$$(O_2 + \varepsilon\delta + 2H_2) \rightleftarrows (2H_2O + \varepsilon\delta).$$

The brackets are added to indicate that a complex system is involved in each case.

The argument may be extended even to explosives. We know from Gattermann's work that the stability of

nitrogen chloride depends upon its purity. In firing cordite—a mixture of cellulosic and glyceric nitrates—not a little of the unburnt material is often projected from the gun in the form of perfect rods much reduced in size. The explosive is not shaken to pieces molecularly but just burnt away at the surface and we have to picture to ourselves the long-despised little ee's or ed's bombarding this with incredible activity as the charge is slowly fired—slowly in comparison with the intra-molecular activities of the explosive system.

A horribly pedantic jargon has been piled up around ethylic aceto-acetate and other compounds which lead a double life, beginning with the word *tautomeric*: an unnecessary invention, Berzelius having rightly assigned *metameric* to such use. They were long represented as not knowing their own minds for two seconds together—strange to say, no Ostwald ever coined the term *Lunoids* for them—as ever undergoing an internal molecular change at their own sweet wills. It has always been clear that little εδ was at work. Groves and I took this view in several instances in writing our (Miller's) *Organic Chemistry* (1880); and Lowry, in my laboratory, has given the most complete proof of the thesis. Recently, it has been found that either of the two metameric (isodynamic) forms of the aceto-acetate may be obtained at will by observing certain precautions—mainly, be it noted, by using quartz instead of glass vessels.

I have not yet reached a terminus. If logical and we have faith in our prophetic powers, we may project our minds into the future and foresee the time when it is admitted that liquids and also solids are not as we see them. Baker is already leading the advance into this field. By drying benzene, he has raised its boiling point above that of water—if indeed the explosive behaviour at the higher temperature can be characterised as

"boiling." He has obtained similar results with carbon bisulphide and other liquids. Carnelly's dream of hot ice was perhaps not the absurdity it was deemed to be at the time! Benzene boiling at 107° or mercury at about 450° would have been scoffed at equally. Benzene and similar liquids which are not miscible with water are not easily dried but once dried they are not easily wetted. Baker being a veritable wizard has been able to boil off water through dried benzene. Modest in manner and modest in statement, he has made far too little impression upon our cloth; no Teutonic Boswell has log-rolled his progress, no special Journal has been founded to acclaim the peculiar joys or drawbacks of the dry state in chemistry, no Act of Congress has been passed to provide for its operation. The main reason probably why the prophet has been insufficiently honoured even in his own country is the fact that we chemists are educated into being the dullest of drones—without imagination. We cannot remain dry ourselves, even in the U.S.A.: therefore, apparently, we have neither belief nor interest in the dry state, except as one to be avoided; we only subconsciously realise perhaps that you cannot get on in it; presumably it is one involving the death of chemical change, as it is of all artistry, because of the inanimate life the molecules enjoy during drought.

The Catalyst

Having considered the conditions which determine the occurrence of chemical change, let us now pass to those which hasten its progress. The interaction of hydrogen and oxygen is promoted by platinum in any state of division but more especially when it is very finely sub-divided, as in the spongy platinum first used for the purpose by Döbereiner in 1823, although Humphry

Davy had previously (1817) noted the inductive effect of the metal in the massive state.

Döbereiner, as Faraday wrote in 1833,

> refers the effect entirely to an electrolytic action. He considers the platina and hydrogen as forming a voltaic element of the ordinary kind, in which the hydrogen, being very highly positive, represents the zinc of the usual arrangement and like it, therefore, attracts oxygen and combines with it.

The only essential condition, as Faraday insists, is a clean metallic surface. As he recognised,

> The effect is evidently produced by most, if not all, solid bodies, weakly perhaps by many of them but rising to a high degree in platina. Dulong and Thénard have very philosophically extended our knowledge of the property to its possession by all the metals and by earths, glass, stones, etc.; and every idea of its being a known and recognised electric action is in this way removed.

What could be better, too, than the following?—

> All the phenomena connected with this subject press upon my mind the conviction that the effects in question are entirely incidental and of a secondary nature; that they are dependent upon the *natural conditions* of gaseous elasticity, combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination, though often assuming the condition of adhesion; and which occasionally leads under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction.

The modern work of Hardy, Langmuir and others is

justification of the view that condensation at solid surfaces is the outcome, not of a mere mechanical cohesion but of an attraction due to residual chemical affinity and therefore selective—in fact, a function of structure. The peculiar activity of platinum seems to be due to the fact that it is highly attractive of both hydrogen and oxygen —whether and to what extent it combines with them to form an "oxide" when exposed to the two gases is open to question. Willstätter has argued that the presence of some oxygen in platinum sponge is essential to its activity as a hydrogenating agent and he assumes that an unstable compound with both elements is formed. Faraday's observation that, although the plate is less readily cleansed when made the negative pole in diluted sulphuric acid, a platinum plate at which hydrogen has been evolved, when clean, is equally active in promoting the interaction, would seem to preclude the presence and need of oxygen, unless it be that the formation of the oxide postulated by Willstätter take place immediately, by partial displacement of hydrogen, on presentation of the clean metal to the gas; also the fact that most if not all solid bodies are in some degree active, is against the oxide view but the gradual corrugation of the solid metal and the expansion of palladium as it is charged must not be overlooked as favouring it.

For the present argument, this is a question of minor importance. The main function of the platinum surface would seem to be to capture and raise the concentration of the interacting substances; not to induce change but to hasten it by this increase of concentration. The determinant is as necessary as in the ordinary case of interaction of the gases in its absence, as without it no electrolyte would be present. The problem has not yet been submitted to any refined study but it is known that moisture favours the action.

I am thus brought to the definition of a Catalyst* as something different from a Determinant and to accept the statement, which is commonly stressed, that it is an agent which accelerates a change in being. Unlike the Determinant, however, the Catalyst is not an electrolyte but merely a solid superficies at which the interacting substances become condensed and therefore of increased concentration; hence the acceleration of the interaction and hence the value of its aid.

In the mind's eye, from Faraday's massive plate to the most minute speck of platinum mounted upon a Messelian asbestos support, the change in size and increase in activity is continuous and doubtless in correspondence with the increase in surface area; the greatest activity would be that of molecular fineness. The speck, however, must remain a speck: it must retain its particulate character; in solution, the molecules are too often married with the solvent, their distribution is too uniform, to permit of an excited rate of change.

The activity of the catalyst would seem to be due to the operation of the force of residual affinity; on no other assumption can we well understand the preferential activity of various catalysts. The work of Hardy and Langmuir especially has afforded proof that molecular structure is a determining factor and that a single layer of molecules can cover and effectively occupy a solid surface. The molecules in some way become ranged in accordance with their structure. Chemists have long thought of the carboxyl radicle in acids as the active part of the molecule and it is no surprise to have proof given that when a fatty acid is spread out upon water the molecules become ranged in the film in serried ranks,

* I believe I introduced the term in 1885. *Catalyser* (*catalyzer*) is a word without euphony to my ear and I would specially deprecate the use of the verb *to catalyse* or any verbal form of the term.

like porcupine-fishing floats in a stream, only the carboxyl radicle dipping into the liquid; the argument may be extended to an oiled solid surface.

The character of the surface also plays its part. Hardy has definitely shown that glass, metal and various kinds of composite material of the ebonite class behave differently. We can but imagine that the structural character comes into play and that centres of attraction may be offered. No other explanation can well be given of the entirely selective activity of the colloid catalysts—the enzymes, the potent agents of change at the root of all vital activity. It is commonly stated that these fit their compatible hydrolytes as a key fits a lock; the hypothesis was put forward by the late Prof. Emil Fischer, long my venerated friend; as he has been regarded as a super-authority, not only in Germany where it is customary to worship the words of professors but by chemists generally, the suggestion has been made one of our chemical shibboleths. Infinitely gullible we are, as Carlyle has said. The suggestion does not bear thinking about, charming though it be as a literary parallel. A key is something entirely different from a lock—something which fits into its blanks. Blanks are unknown to us in our chemical locks. The fit cannot well be other than that of similarity: in some part the enzymic complex must be so like the compatible hydrolyte that the two fit together when superposed; we are therefore driven to think of this active centre as the hydrolyte itself gathered into the structure of the complex. My son and I have long advocated this view.

The influence of proteid colloids other than enzymes as catalysts has been little studied.* The production of

* The attempt has been made by the school that dubs itself "colloid" to read into the term the sense of particulate—of very finely divided matter in suspension in a fluid. Nothing was farther from Graham's mind.

I would urge that the term colloid should be used only in its etymological

hydrazine from ammonia and hypochlorite, according to Raschig, is promoted by the presence of a little glue, but it is found, I believe, that all glues do not equally serve the purpose. If so, is the difference due to some structural peculiarity? It is conceivable that the interaction may involve the intervention of a protein chloramine? If so, structure might tell.

In addition to directly active catalysts—catalysts which exert a definite attractive effect upon substances whose interaction they promote—there is conceivably a neutral class, effective through the agency of the specially active layer of simple hydrone molecules deposited at their surface.

Hydrone and Water

Progress has too long been stayed by the fiction that water is represented by the symbol OH_2—by the failure to recognise that it is a "mush" of molecules of several

sense and confined to substances such as Graham contemplated—substances opposite to the so-called crystalloids in the scale of solubility.

Then that a distinction be drawn between actions in solution and those at particulate surfaces.

The passage of the colloid from solution into the particulate state probably involves far more than meets the eye, even that of imagination, to-day. McBain's fascinating studies of soaps have brought to light the existence of a tendency similar to that apparent in compounds such as the cobaltamines and other complex salts, in which one or more of several negative radicles is lost to view. In the soaps, several primary molecules of the salt are merged into an aggregate in which the alkali is in large part hidden away. We have to remember that even acetates have a tendency to take on a more complex form than that of the simple molecule. It is possible to think of a wheel-like arrangement of the molecules, in which most of the carboxylated groups are at the hub, the hydrocarbon radicles ranging outwards like spokes. The coagulation of colloids may well involve the formation of aggregates, in like manner; the production of a jelly is conceivably due to the interlocking of such polymerised molecules, water filling the waste spaces. As Wilder D. B. has the goodness to say: "For the moment it looks as though the organic chemist were the safe man to follow," rather than the adsorbist. Yet such an explanation can scarcely be given of the agglutination of micro-organisms under some special conditions which we cannot yet appreciate; the primary change, in these cases, may be in water.

degrees of complexity.* Unfortunately, we can only distinguish one at present, the simplest, that of hydrone, OH_2, probably always a minor constituent of water. Bragg's recent work rather favours the view that ordinary ice is a benzenoid complex in which six hydrone molecules are conjoined. I have long been of the belief that water is to be thought of as a mixture of hydrone with several polyhydrones of the polymethylene type.

If we could be logical, we should only apply the term water to the liquid substance, never to that symbolised as H_2O. We have as little right to think of this as water † as we have of the various polymethylenes as methylene.

* The rapid increase in the rate of chemical change as the temperature of a solution is raised, it may be suggested, is mainly due to the changes which water itself undergoes—to its increasing activity.

† When Mr. Walcot has exhausted his imaginative power in depicting Roman and Persian subjects, he will perhaps find a worthy stimulus to his needle in an allegorical presentment of the new Babylon science is building. I said much of our abuse of our language in 1894, in my first Presidential Address to the Chemical Society. As Secretary, I had had some influence in securing uniformity and clearness of expression. To-day, there seems to be no check to lawlessness—no clear understanding of law, no desire to arrive at and obey the law. Proceedings under the Safeguarding of Industries Act show that we must spring-clean our vocabulary and give thought to our words. Why do we so carelessly use Interaction and Reaction indifferently, when the former expresses our meaning and the latter does not? Why are we not satisfied to speak of chemical agents, instead of reagents? The medical man is content with "therapeutic agents." Why introduce "reactant"—an unnecessary and un-English word? Our object should be to use words as near as possible to those in popular use, if not those in actual use: our desire being to live on terms of intimacy with the public. Why coin new words when old ones will suffice?—Adsorption would be a proper word to introduce, if a new word were necessary; several popular words suffice to convey the idea underlying its use. It is strange to the common ear and to the novice. If we are to coin new words, they should suit the genius of our language; no language is so hospitable to foreign intruders, yet it cannot admit every stranger that may call in. To get over the difficulty arising from the alternative use of absorb and adsorb, it is proposed to omit the prefix; but sorb is a word without dignity and the attempt to introduce it should not be countenanced. The introductory "But" is a mild offender compared with it. Then why so un-English a term as ionic *micell* when aggregate gives complete expression to the underlying idea: the word carries no crumb of comfort to the British ear; and what will it become in America—My-y-sell? Anything may happen to such a word. It is time some sense of eternal fitness,

The Pseudo-Physical School has been so impassive and impenetrable by ideas, so intellectually pachydermatous, that it has never given heed to the composition of water. The treatment of the problems of solutions by the school has therefore been purely empirical and of small value. The main object has been to force agreement with a formula; this satisfies the mathematical mind but not the free-spirited chemist striving to see within and to dissect out the active factors. We are often told that a return to the land is now our one hope of salvation as a people—in any case our ultimate fate. Let us chemists recognise that we can only abide in chemistry and let this be to us a word of real significance, of broad and intensive meaning. A chemist, to do effective work, must be a chemist and not a mere bit of one, still less a formula-seeking mathematician.

To begin with, we must purify and simplify our nomenclature and use only words of clear import. We must arrive at an understanding as to the meaning to be given to the term solution. The term solid solution is a contradiction in terms; Colloid solution is equally bad; in a crystalline solid mixture there cannot be that evenness of distribution which is the characteristic of a solution; motion must be constrained and limited, not illimitable; there cannot be that exercise of affection between solute and solvent, that compatibility of temper due to oppositeness of character, which is at the root of solubility and dissolving power, which leads to short marrying long, to beauty mating with ugliness.

if not of the ridiculous, were infused into the scientific mind—if we wish to secure public sympathy. Still:

> Oh ye who tread the Narrow Way
> By Tophet-flare to Judgment Day,
> Be gentle when the heathen pray
> To Buddha at Kamâkura.

Determinant and Catalyst

This brings me to the final distinction I desire to make between Determinant ($\epsilon\delta$) and Catalyst (κ).

The one is active in solution, the other in suspension; in the one case the distribution of the components is even; in the other it is uneven and local, the catalyst being a surface-centre towards which the interacting substances are attracted.

In the presence only of a determinant, the rate of change is in accordance with the sacred Law of Mass Action, which is ever subject to modification, however, owing to changes in the medium conditioned by the alterations in molecular character and complexity which attend all interactions, just as human laws are always being modified by circumstances.

In the presence of a catalyst, the action is not in accordance with the nominal concentration but much more rapid and nearly at a linear rate over the greater part of the period of change. Unfortunately, the action of catalysts, especially of enzymes, is often obscured by secondary actions and the assumption that all chemical change must be subject to the mass action law has gained such credence that almost everywhere the temptation to twist the results to this interpretation has been irresistible. There has, however, long been a suspicion that enzymic hydrolysis takes place mainly at linear rates, so long as disturbing influences are inoperative; it is permissible to say, I think, that the work done in my laboratory, especially that with urea and the enzyme urease, has raised this to a certainty, confirmed as it has been, in the most striking manner possible, by the observations made by Drs. E. F. Armstrong and Hilditch on the hydrogenation of oily fluids in presence of very finely divided metallic nickel.

Let me cross the t's in this section by saying that if, we desire to give expression to the action of a catalyst in writing an explanatory equation, this may be done as in the following example:

$$O_2 + \varepsilon\delta\kappa + 2H_2 = 2H_2O + \varepsilon\delta\kappa.$$

By associating the symbol of the electrolytic determinant with that of the catalyst, the fact is brought out that the former is necessary and that both factors are concerned in the operation.

Hydroxylation not Oxygenation

The formation of hydrone from hydrogen and oxygen is but imperfectly expressed even in the equation:

$$O_2 + \varepsilon\delta + 2H_2 = 2OH_2 + \varepsilon\delta;$$

it is true unusual attention is paid to the character of the process but this is not fully developed as an electrolytic event.

When writing my *Introduction to the Study of Inorganic Chemistry*, published in 1874, although I was grossly ignorant and inexperienced, I was beginning to think. Discussing the formation of acids by the oxidation of the corresponding aldehydes, having assimilated Avogadro's theorem and knowing the formula of oxygen, which few did at that time, I wrote (p. 241):

$$2R'{\cdot}COH + O_2 = 2R'{\cdot}CO(OH).$$

In a footnote I added: "Perhaps

$$R'{\cdot}COH + O + OH_2 = R'{\cdot}CO(OH) + OH_2,$$

i.e., the reaction is one of double decomposition, H being replaced by OH and does not consist in the mere addition of oxygen." In Miller's *Organic Chemistry* (p. 417),

published in 1880, this conception was logically extended to cases of oxidation generally.

I had not then consciously developed a consistent electrolytic conception of chemical change, yet I was approaching it and had foreseen that the oxidation process is to be interpreted as primarily one involving hydroxylation.

It may safely be asserted, taking the facts generally into account, that when acidified water is electrolysed, hydrone molecules are primarily resolved not into oxygen and hydrogen but into perhydrone (hydrogen peroxide) and hydrogen :

$$\begin{matrix} H & . & . & . & OH \\ H & . & . & . & OH \end{matrix} = H_2 \quad . \quad . \quad . \quad (O_2H_2)$$

The dots stand for the little $\varepsilon\delta$'s, the electrolytic systems which carry H and OH at their terminals. The perhydrone, maybe a sulphonic-perhydrol, is decomposed at the electrode face. How ? Not by mere contact with the chilly metal ; the process resorted to is a warmer one, I believe, involving hydroxylation of the perhydrone :

$$HO{\cdot}OH + \varepsilon\delta\kappa + HO{\cdot}OH = HO{\cdot}O{\cdot}OH + OH_2 = \varepsilon\delta\kappa$$

and when the hydroxyls are crowded together as they are at certain strengths of sulphuric acid or when currents of relatively high density are applied to the solution, probably still higher perhydrones are produced by a similar process.

Oxygen and ozone appear to be the products of the breakdown of these perhydrones.

A wicked and perverse generation, to the present day, we teach the poor student that when water is electrolysed —acid is added, to make it conducting, we say—it is resolved into hydrogen and oxygen ; occasionally a reference is made to by-products, never to the probability

that the oxygen is a by- or secondary product. Endless talk about hydrogen and hydroxyl ions is probably indulged in and the student carries the scars of these through life, though nothing more; fiction is always preferred to fact, in reading.

What is true of electrolysis is true of oxidation phenomena generally.* Hydrogen is first burnt to perhydrone (hydrogen peroxide); the oxygen is merely hydrogenised. In turn, the perhydrone molecule serves as the oxidant, so that the oxygen molecule is broken down in two stages; there is no reason to think of atomic oxygen as ever engaged in the operation. Were it not that the mystic word "ionised" is now grafted into our being, we should think without difficulty in terms of molecules and be rational.

Hydrocarbons behave, in general, as hydrogen.

Carbonic oxide is peculiar in this as in most other respects. It is commonly recognised not only that this gas cannot be burnt dry but that the rate of combustion rises as the amount of hydrone in admixture with it is increased, up to a certain point; hydrone apparently plays a peculiarly active part in its combustion, primarily through incorporation into its being. In fact, it is difficult to think of hydrone as active in conjunction with carbonic oxide except by giving rise to formic acid; the two molecules cannot well grip each other at all with any other result. Carbonic oxide, under ordinary conditions, is an alert molecule which cannot easily be caught; tamed at the surface of a catalyst it is docile enough. A mixture of carbonic oxide and chlorine must be well sunburnt to induce interaction but an active charcoal will induce the immediate pairing of the gases. Faraday found that unheated clean platinum was without sensible action on a mixture of carbonic oxide with oxygen;

* Compare my "Studies on Oxidation," *Journ. Soc. Chem. Ind.*, 1913, 391.

further, that in presence of any considerable proportion of carbonic oxide, hydrogen and oxygen were indifferent to each other at the metallic surface. It is therefore to be supposed that the carbonic oxide molecules, having the greater affinity for platinum, cover up its surface against hydrogen. Faraday's observations were confirmed by Groves' later study of the gas battery. It is an unfortunate fact that carbonic oxide and oxygen cannot, as far as we know, be usefully associated in an electrolytic circuit; if the disability could be got over and economically, how golden might the future of industry be.

Given the initial production of formic acid, all else in the behaviour of carbonic oxide is clear. The oxidation of this acid presumably involves the formation in the first instance of a perhydrol (peracid) which breaks down on hydrolysis into carbon dioxide and hydrone (*cf.* p. 107):

$$\mathrm{HCO{\cdot}OH} + \begin{array}{c}\mathrm{OH....H}\\ \\ \mathrm{OH....H}\end{array} + \begin{array}{c}\mathrm{O}\\ |\\ \mathrm{O}\end{array} = \mathrm{HCO{\cdot}O{\cdot}OH} + \mathrm{OH_2} + \mathrm{O_2H_2}$$

$$\begin{array}{l}\mathrm{H{\cdot}CO{\cdot}O\,..\,OH}\\ \qquad\;\downarrow\;\;\uparrow\\ \qquad\mathrm{HO\,..\,H}\end{array} = \mathrm{OH_2} + \mathrm{CO_2} + \mathrm{OH_2}$$

I call attention to these operations in order to make clear the point that the "Sweet to the Sweet" principle prevails in chemistry, as in life. Oxygen seeks oxygen but falls a prey to hydrogen by the way. Only on this assumption can we understand the manner—sometimes dubbed peculiar by the thoughtless—in which the oxidation of carbon compounds is effected. In the case of the fatty acids, the candle is mainly burnt not at both ends but at the carboxyl wick, which is necessarily attractive as an electrolytic centre. Apparently the perhydrol that is formed then proceeds to curl its hydroxylic-tail and, like the whiting, the CH_2 radicle next but one to the carboxyl group swallows the hydroxyl

at its tip; then casting off hydrone, it is reduced to a weakened state, in which it soon falls a victim to further hydroxylic attack. In plain symbols—

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OH$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}OH$$
$$CH_3{\cdot}CH{\cdot}CH_2{\cdot}CO$$
$$|\!-\!O\!-\!| + OH_2 = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}OH$$
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OH.$$

Dakin has written a special monograph on the subject —but without discussing the process: such is the advanced state of our chemistry. Ions to right of us, ions to left of us, onward we stumble but look, let alone see, where we are going, rarely. Why the tail is swallowed at the third carbon atom history does not tell: the future historian will probably recognise that it is a consequence of a structural peculiarity innate in the carbon chain. The agent also at times is not without influence upon the result; probably it alters the length of lash of the tail.

I have yet to withdraw one reputed catalyst from your sight—the ferrous salt; to put it in its proper place, that of a mere determinant, a little εδ.

By hypothesis, perhydrone is not an oxidising agent: like water, it is not an electrolyte. When coupled with an iron salt, it becomes active, we may assume, in virtue of the formation of a perhydrol which is an electrolyte in solution:

Ferrous sulphate   Ferrous sulphate perhydrol

This compound may be produced, be it noted, starting with oxygen. The perhydrol, moreover, cannot only serve as an "oxidase" but also as a "catalase": it can

oxidise perhydrone itself and so determine the liberation of oxygen.

The idea that oxygen acts *directly* as an oxidising agent is so fixed in our minds that it is with difficulty put aside; yet it is one to be discarded.

Directed Oxidation

We have also to realise that hydroxylation may take place in the absence of oxygen—under the influence of reducing agents. This process is one of special importance as playing a determining part in vital phenomena, in fermentation, for example. It is that which renders anaerobic life possible. A specially interesting case has been dealt with recently by Gowland Hopkins, Morgan and Stewart, who have studied the action of a peculiar agent in milk which induces the oxidation of both xanthin and hypoxanthin in presence of a reducible substance such as methylene-blue, for which oxygen may be substituted. The agent in question is not a mere determinant like ferrous sulphate but a catalyst, as change proceeds under its influence at linear rates. As its activity is confined to the two bases mentioned, the catalyst is to be regarded as an enzyme, the more as it is destroyed by heat.

The oxidising agent acts only indirectly as depolariser, the active hydrogenating agent in the oxidation process being the hydroxyl of hydrone liberated in an electrolytic circuit in the following manner:

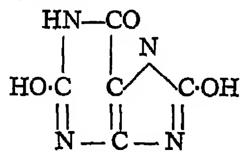
$$\begin{array}{c|c|cc|c|cc}
O & H\ldots OH & & OH & \ldots & OH & \\
| & & X = & | & & & X \\
O & H\ldots OH & & OH & \ldots & OH &
\end{array}$$

X is the oxidised material. Methylene-blue (or other reducible substance) may be set in the place of oxygen in this expression. The only distinction to be drawn

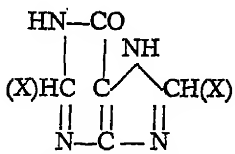
between them is that oxygen has double the value methylene-blue as a reducible substance, the perhydro produced at first being itself reducible to hydrone.

The remarkable fact has been established, by Hopki and his fellow workers, that with the aid of methylen blue the two bases are oxidised (to uric acid) at mol cularly equal rates, twice the amount of work being do upon the one as upon the other : it is therefore necessa to conclude that the two oxidisable centres in hyp xanthin are in a single circuit.

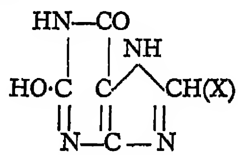
The striking similarity in the two bases and uric aci is brought out clearly when their formulae are writte in the following way, X being the centre at whic hydroxylation takes place :



Uric acid



Hypoxanthin



Xanthin

As the oxidase can influence or direct attack at tw centres simultaneously in hypoxanthin, it is probabl that the enzyme fits upon a large section if not th whole of the molecule.

An enzyme which could thus act may be imagined containing as active component uric acid itself; thi might be compatible with both molecules, as the CH group to be oxidised would probably be no obstacle t its fit, whilst the presence of NH in place of O in adenin and guanine would certainly be an interference. It i

possible to think of such an enzyme becoming perhydroxylised under the influence of the hydrogen acceptor and the product as inducing in turn the hyrdoxylation of one or both sensitive centres in the two bases. The effect on hypoxanthin would be like that of using two voltaic cells in series instead of a single cell of about half their joint electromotive force.

In ordinary alcoholic fermentation, assuming that the glucose molecule be primarily resolved into two molecules of glyceraldehydrol,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH)_2$$

both a highly reducible and a highly oxidisable substance, the reduction of the one molecule may be supposed to take place, directly or indirectly, in virtue of the hydroxylation of the other.

The results obtained by Hopkins, Morgan and Stewart are also of special interest in connection with the oxidases so frequently met with in plant and animal fluids; the evidence that these are enzymes has hitherto been inconclusive, though from their specific behaviour it appeared probable that at least some of them were.*

Such enzymes should be distinguished from those which simply induce hydrolysis of a single molecule. These latter may be termed *homolytic*, whilst those which promote hydroxylation by the co-operative action of two distinct molecules, the one reducible and the other oxidisable, may well be termed *heterolytic*.

I thus end my discussion of chemical change upon a natural note and pass to

Sulphuric Acid

yet only again to voice a complaint of inattention, if not of ignorance. Over fifty years ago, when fellow

* I am now all but persuaded that the oxidases are mere catalysts, not enzymes. I was guilty, I fear, of romancing in these paragraphs.

students, Horace Brown and I were Frankland's " Versuchsthieren," used in imagining graphic formulae, to test the application of the then new practice of such exercise; we played the game much as that of noughts and crosses is by children, in accordance with certain very elementary rules. To-day we cannot express the structure of sulphuric acid with any less uncertainty than Horace Brown and I did in those distant days of our early innocence.

What *is* the structure of sulphuric acid? We simply do not know. What indeed do we mean by sulphuric acid? It is premature to ask the question until we agree in our definition of an acid. To get this fat out of the fire will be no easy matter.

I ask you to face the facts. It matters little how much knowledge we have; it can avail us little if we are not alive to our ignorance of things fundamental.

The Acid Function

I have been much struck of late by the frequency with which in examination papers of schoolboys *oxygen* is referred to as a misnomer. In a French scheme for the reform of the nomenclature of inorganic compounds, brought forward at the Lyons Conference a few days ago, the compound formulated HCl is referred to as a hydracid and given the name " acide chlor-hydrique "; we often go one worse, calling it hydrochloric acid, seeing that there is no " chloric " about it. Such base use make we of our perversity.

Sacré nom de Lavoisier! Oxygen a misnomer! Hydrogen chloride an acid! Asticot would say: *C'est abracadabrant!* Are we not told that when the *Quartier Latin* so calls a thing, there is no more to say? Is it not truly written and for evermore: " La Chimie est une Science

Française, *Elle fut constituée par Lavoisier*," etc.? In designing the word Oxygen, Lavoisier rose to the greatest height of his unparalleled genius. Not only is the word a monument to his astounding insight into chemical phenomena, to his philosophic power; it is also proof of deep philological feeling and acumen, as well as of his sense of the beauty of words. Think of the astounding step he took, after his instant appreciation of Priestley's discovery, in translating the old nonconformist's ponderous reminder of the doubtful past of our science conveyed in the name *Dephlogisticated Air* into an all significant word of the aural and lingual perfection of *Oxygen*, paralleled only, to those who have an ear for nordic harmony, by *Sauerstoff*, which unfortunately we cannot translate into English, though *Sauerkraut* sounds just as well in our tongue as in German: stuff unfortunately is gone out of fashion in our language; at best we associate it with either nonsense or dreams.

Lavoisier did more—he atticised our Science for all time; yet the scribes and literary Goths, uncultured in all but their own works, scoff at us as Greekless! The while they are unable to interpret a word so all-meaning as Oxygen or construe a single passage in our writings. Don't let us think of Lavoisier merely as a man who heated mercury in air and lost his head; think of him as the pioneer who not only sought to put system into the souls of chemists but also tipped their tongues with harmony.*

* This is equally true of the name Lavoisier gave to the companion of oxygen in air. The passage in which he states his reasons for terming this *Azote* is of extraordinary interest.

"Les propriétés chimiques de la partie non respirable de l'air de l'atmosphère n'étant pas encore très-bien connues, nous nous somme contentés de déduire le nom *de sa base* de la propriété qu'a ce gaz de priver de la vie les animaux qui le respirent, nous l'avons donc nommé *Azote*, de l'a privatif des Grecs et de ζωή, vie; ainsi la partie non respirable de l'air sera le gaz azotique.

"Nous ne nous sommes pas dissimulé que ce nom présentait quelque

In my early days, the Berzelian sun was not yet set. Oxides were of two classes, acidic and basic and these combined to form a third, the salts. Debus and Williamson

chose d'extraordinaire; mais c'est le sort de tous les noms nouveaux; ce n'est que par l'usage qu'on se familiarise avec eux. Nous en avons d'ailleurs cherché longtemps un meilleur, sans qu'il nous ait été possible de le rencontrer; nous avions été tentés d'abord de le nommer gaz alcaligène, parce qu'il est prouvé, par les expériences de M. Berthollet, que ce gaz entre dans le composition de l'alcali volatil ou ammoniaque; mais, d'un autre côté, nous n'avions pas encore la preuve qu'il soit un des principes constitutifs des autres alcalis; il est d'ailleurs prouvé qu'il entre également dans la combinaison de l'acide nitrique; on aurait donc été tout aussi fondé à le nommer principe nitrigène. Enfin, nous avons dû rejeter un nom qui comportait une idée systématique."

It is unfortunate that we did not follow the French in preferring *Azote* to nitrogen—the name is so perfect and significant—as applied to the inert gas in air: the contrast would have been complete had the active constituent been termed *Zote.* In some way this latter word seems to lack force without the privative α. Still, it would not be difficult to accustom our ears to Zote and Azote; we should then be able to draw the distinction that is so desirable between the two chief materials of air and their constituent stuffs symbolised by O and N, which represent ideals: Lavoisier clearly intended the names Oxygen and Nitrogen to apply to these ideals; he as definitely draws a distinction between azotic gas and azote, in the above passage, as he does between oxygen gas and oxygen in giving his reason for the adoption of this name.

"Nous avons donné à la base de la portion respirable de l'air le nom d'oxygéne, en le dérivant de deux mots Grecs, 'οξύs acide, γείνομαι j'engendre, parce, qu'en effet une des propriétés les plus générales de cette base est de former des acides en se combinant avec la plupart des substances."

The distinction is again made clear in the following passage:

"De la Décomposition du Gaz Oxygène par les Métaux." Lorsque les substances métalliques sont échauffées à un certain degré de température, l'oxygène a plus d'affinité avec elles, qu'avec le calorique: en conséquence toutes les substances métalliques, si l'on en excepte l'or, l'argent et le platine, ont la propriété de décomposer le gas oxygéne, *de s'emparer de sa base* et d'en dégager le calorique."

Lavoisier's clearness of vision in seeking for a name other than azote, significant of the chemical character of the element, is very remarkable. Had he known of the amines, he would surely have proposed *Aminogen* and we should then have been in possession of two of the most perfect names possible.

The quickness of the Darwinian uptake of ideas is well shown by Erasmus Darwin's early use of Lavoisier's term in Canto IV of his poem "Economy of Vegetation."

"Sylphs! from each sun-bright leaf, that twinkling shakes
O'er Earth's green lap or shoots amid her lakes,
Your playful bands with simpering lips invite
And wed the enamour'd Oxygene to Light."

spoke of the *oxide* formulated SO_3 as sulphuric *acid*; the compound formulated H_2SO_4 was hydric sulphate. Messel always spoke of this latter as *monohydrate*—a survival of the significant Berzelian nomenclature.

Some disturber of the peace then came along and gave unnecessary prominence to the least of atoms, Hydrogen. A fashion arose of teaching chemistry, instead of allowing students to learn it; so it was necessary to furnish with definitions the poor mummers who taught. For text-book purposes, an acid was defined as a compound containing hydrogen displaceable by metal through the action, if not of the metal itself, of a base, a miserably thin description subject to many more exceptions than the oxygen rule of Lavoisier, if indeed there be any to this latter. There is none, if the acid formed in water by the addition of hydrogen chloride be in truth chlorhydric acid, $HCl{\cdot}OH_2$, as I contended so far back as 1885.

When hydrogen is turned out from an acid, it is in no direct, open and honest way: the more stalwart metal is brought in *sub rosa* at the stage door and is effective owing to the superior attraction it offers to the *oxygenated* radicle of the acid: in symbols:

$$\text{Neg.}\left|\begin{array}{l} H\ldots HSO_4 \\ H\ldots HSO_4 \end{array}\right| Zn = \text{Neg.}\left| H_2 \right| \begin{array}{l} \ldots \\ \ldots \end{array} \left|\begin{array}{l} HSO_4 \\ HSO_4 \end{array}\right\rangle Zn$$

We are agreed that in chemistry we must rely upon formal definitions: no single definition based upon behaviour is of universal application. No acid so-called functions as an acid *per se*. The compounds *named* acids are all inert—for the simple reason that they cannot conduct electricity, all chemical change being electrolytic in character. This could be asserted fearlessly in Faraday's time; how much more then to-day, now that we worship

the electron and regard it as concerned in and guilty of every chemical crime.

The acid takes form only when water is brought to the rescue of the dielectric: as we know, when a man's married, then trouble begins; what happens when a dielectric marries water has long been a subject of debate. Perhaps debate is a wrong term to use. Creeds are not established upon a basis of debate: they are accepted as faiths by adoring, unreasoning, credulous believers, in response to dogmatic assertions. In the early 'eighties, a young prophet arose who appears to have had some training in mathematics and physics but to have acquired no feeling for chemistry; he preached a gospel in which the acids were described as degenerating into the most abandoned of libertines, as becoming drunk with freedom, when cast into solution.

From this time on, the wandering hydrogen atom became in itself the personification of acidity—it is true it was featured as in the leading strings of an adoring opposite positive charge but the bond was admittedly of the weakest and the loose partnership was subject to constant change. The youthful propagandist was properly told by his master that he did not know enough to deal with so serious a subject and that he deserved to be smacked and put back into the nursery; had he been put into a *camisole de force* the world would have been saved much pother and many printers' bills. Unfortunately, as prophets too often are, he was taken at his own valuation and seriously; it was not his fault but a consequence of our lack of logic, of the survival of our primitive habit of yielding obedience to priests and sorcerers.

As Mr. Arnold Bennett somewhere says, we need to have "an ironic realisation of the humanity of human nature." Science is a new habit which does not fit our

human constitution; our mental machinery is a congeries of mechanisms which are only imperfectly correlated; heredity makes us dogmatists and prime worshippers of the Idols of the Theatre. My objection has always been not to the speculation itself but to the maladroit zeal with which it was spread, the unscientific way in which it was rammed down our throats and all discussion burked by people like Ostwald, who obviously did not know what they were talking about and disregarded the findings of chemists in general. Many of the contentions were not only irrational but the ignorance displayed—particularly in the discussion on indicators—has often been astounding; the work put forward was biassed and superficial. Unfortunately, the physicists have not helped us; they have often smiled at our ionic rhapsodies but I have seen no evidence that they have regarded them seriously.

The great chemical blunder made by Arrhenius and his worshippers was in regarding water as hydrone and in representing hydrone as behaving altogether differently from the allied hydride, hydrogen chloride—by their assertion that when the two compounds were mixed, whilst the molecules of the one underwent practically no change, those of the other fell almost entirely to pieces. No reasonable explanation of the suicide was ever offered. Even that great genius van't Hoff, a giant among the pigmies, was carried away by the seeming agreement of fiction with fact. Evil communications corrupt good manners; had he kept other and higher company he would not so easily have been led astray, but his vanity was tickled by the way in which his osmotic dreams were apparently made true by "ionic" coincidences. Had he but witnessed a scrum on a football field and considered its applications in chemistry his vision would have been clearer. Unfortunately, he paid

no attention to water and yet he loved beer. The Arch-Ionian prophet, perforce of his Scandinavian heredity, was necessarily a Hydrophobe and put no measure of aqueous humour into his Koran. Never yet has justice been done to water, least of all in the U.S.A. Mathematician and physicist, rather than chemist, van't Hoff lacked just that element of feeling, the artist's practical sympathy with his subject and devotion to his studio; we must never forget that the laboratory worker is an artist and that, as a rule, practice comes first; so-called theory is usually but brought to the aid of practice in justification of its acts. This is true of agriculture throughout time and of industry to-day. The fancied explanations that have been given need not be taken too seriously; tentative and provisional for the most part, they but help us on our way and we must often be content to retrace our steps, recognising that the alley up which we are led is a blind one; the exercise, however, serves to keep us fit and is a preparation for the next excursion. Everest is not climbed in a year; many avalanches may wreck us and

> 'Tis not antiquity nor author
> That makes Truth truth, altho' Time's daughter.

One real service the ionic school has rendered in systematising the application of Faraday's beautiful word *ion* to radicles which do not stand upon the order of their going but go, once the chance be given. We now speak of salts generally as composed of positive and negative *ions* and the definition is full of meaning. By implication, it conveys the information that the compound consists of easily mobile radicles. On the other hand, compounds such as chlorethane and chlorobenzene, which do not behave as salts, are sufficiently described as

composed of positive and negative *radicles*—the term radicle having a wider but less definite meaning. The distinction is not absolute but sufficient to justify a line being drawn. Why the positive hydrocarbon radicle should exercise so superior an attraction and keep the negative radicle at home and in order we cannot say. The electron worship of the day is too static and simple a faith to satisfy our longing to explain such mystery.

The second service of the Arrhenists has been in emphasising the difference in the strength of acids and bases, always well recognised but not numerically expressed prior to the advent of the ionic speculation. Unfortunately the service is marred by the way in which the conception has been wrapped up in the term *hydrogen-ion-concentration*, a stilted phrase which is not only caviare to the general public but most misleading. Nothing more was necessary than to distinguish between *acidity* or if you will *apparent acidity*, as meaning quantity of acid, and *effective acidity*, as meaning the proportion of the acid present in the immediately active state. A layman can read such terms, even put some meaning into them and without his ear being offended ; hydrogen-ion-concentration is pure gibberish, a chord that cannot be struck upon " the lyre of language clear." It is just a shibboleth which too often covers a pretence of learning ; unfortunately, its forbidding presence is to be met with everywhere and it is being shouted loudly in the galleries of the new Babel which more than threatens to overwhelm science and deprive it of all public support. Even the brewing world only recently was entertained with talk on *Hydrogen Ions in Beer*. Fancy Brother Bung's joy at such a topic being under discussion—the query of the Bar Parlour : " What new poison be they putting into our swipes ? Is this why beer be now such

poor stuff ?* Hang hydrogen ions, give us a little more body and spirit in our drink." It would comfort them to know that there are no hydrogen ions in alcohol: it occurs to me to ask—Is that perhaps the reason why Glasgow is so fond of petrolised water ?

Necessarily I am reminded here of Samuel Butler's story of the conversation he overheard in an inn, summed up in the remark of the speaker to the barman : " Imagination will do any bloody thing almost." Yes, unfortunately it will, even in the ranks of science—except make us wise.

One unforgivable result of enforcing the doctrine is, that acidity is regarded not as the function of an acid but of just one little bit of the molecule and that split off and away from it ! I have sufficient belief in sulphuric acid to feel satisfied that it has a real sense of its own importance and that it acts accordingly—that its positive and negative radicles are equally concerned, directly or indirectly, in all its actions—always bearing in mind that all chemical interactions are electrolytic manifestations and polar phenomena, never unilateral.

Electrolytic Conductivity

The position to-day is but little, if in any way, different from that of 1851, when Williamson's most remarkable communication *On Etherification* was made to the Chemical Society—remarkable because of the far-reaching character of his inferences and because of his youth and inexperience. By a stroke of genius he laid bare, probably for all time, the conditions in a solution—by drawing attention to the constant interchange of radicles which it was to be supposed must always be going on, to account

* Beer, too, would seem to be a terribly toxic substance from the point of view of "Colloid Chemistry," to judge from a recent essay presented to brewers on the influence of the " dispersity " of the colloid on flavour. We must abolish such moonshine and speak English.

for the state of equilibrium at once established whenever two or more salts are brought together. Williamson appears to have contemplated only an interchange of the radicles, never their free existence in solution. Kekulé afterwards suggested that the interchange was preceded by the association of the interacting molecules, a view I advocated in later years when interpreting the formation of substitution derivatives of benzene.

Clausius, in 1857, to explain the behaviour of electrolytes, first suggested that occasional violent molecular encounters in a solution now and then led to the disruption of the molecules. Arrhenius extended the speculation, by assuming that chemical activity was proportional to the degree of disruption and that specially active solutes, such as the strong acids, were all but entirely dissociated. He thus opened up a path for the mathematical treatment of the subject—by directly connecting chemical activity with electrical conductivity in a more definite way than had Clausius, who was merely concerned with electrical behaviour. He thereby did considerable service, but he and his literary body-slave, Ostwald, followed Clausius in regarding the action of the solvent as merely that of a screen; only later did they hedge in face of our protests. By attributing the "dissociation" to the high specific inductive capacity of the solvent they were but paraphrasing our contention that the change was due to an interaction of solvent and solute, brought about by the residual affinities of the associated molecules: at all times it was useless to argue the point with them on chemical grounds: they would not understand us: a banner with a new device had been found and its possessors hurried on to plant it everywhere—as revolutionaries mostly do, without counting the cost of the doctrine they profess. The one point I am anxious to make is, that whilst we must have

imagination, progress being dependent upon its exercise, we must give it always the controlled and guarded use implied in Tyndall's well-known and immortal phrase. An unscientific use may give us music—indeed genius must often operate in disregard of the rules of science—but science is founded upon imagination controlled and tried.

Probably we can assert as indisputable and all will agree, that in aqueous solutions the ions H and OH are ever on guard at the gates of entry and exit, armed and ready for immediate action on receipt of an electric call. The analogy of a corporal's guard is by no means one that is far fetched ; in this the units are connected by the invisible link of discipline and are the counterpart of an electrolytic system. An interchange of sentries is not effected at random but by a regulated polar process. This, at present, is perhaps as far as we either can or may see. The whole subject is in need of further experimental study from a H. B. Baker point of view. We have not only to learn to use clear and just language but to labour to be clean. In the light of Baker's recent results, I am now inclined to take up a position more absolute than that I adopted 36 years ago, in March, 1885 ; to doubt if there be such a thing as a simple electrolyte—a substance which is an electrolyte *per se* in the pure state. Maybe some day a Baker will show that metallic halides—silver chloride, sodium chloride—are not electrolytic conductors and that metals are the only primary conductors of electricity; we have yet to learn where entire prohibition of impurity will carry us. I foresee a physics very different from the present—no longer a physics of freedom but one of slavery to unrestrained residual affinity (*cf.* p. 60).

We need to study afresh the passage of matter through its several states. It is already recognised, on the basis

of Aitken's observations, that the condensation of hydrone to water involves the presence of "nuclei": the nucleus may act as a catalyst but what of the determinant—is one required? What would be the behaviour of exceptionally purified gases generally in exceptionally cleansed vessels? Might not the Andrew's "critical temperature" be greatly modified? Monatomic molecules of materials such as hydrogen, oxygen, nitrogen, may well persist under "clean" conditions. Rayleigh's observations on nitrogen and R. W. Wood's more recent studies of hydrogen already lend support to the view.

Thus far my dream—I trust I have made clear my vision of the process of change.

Structure and Basicity of Sulphuric Acid

In my days of early innocence, in 1871, I wrote—"Occupied with an investigation into the constitution of sulphuric acid"—as the opening sentence of the first of my Studies on Sulphonation. The subject still occupies a cell in my mind. It is strange that, excepting perhaps soda and not even that before the advent of the Solvay-Mond process, the compound manufactured on a more colossal scale than any other should to-day be a sealed book to us; it contains but seven atoms, which cannot well be otherwise than simply arranged. Perhaps X-rays will soon melt the seal which chemists have so long left intact. It is the old story—familiarity breeds contempt: simplicity is the most difficult of attributes to interpret. The major riddles of chemistry are carbonic and nitric oxides, CO and NO *and* sulphuric acid.

It is commonly ranked as a *bibasic acid*—what precisely does this mean? What valid evidence have we of its structure? Practically nothing of consequence. Graphic formulae such as Horace Brown and I constructed on

paper, out of our heads, 55 years ago, still prevail over fact. Williamson and Odling, having their minds filled with types, derived the acid symmetrically from the double molecule of hydrone,

$$\begin{array}{c} H \\ O \\ H \\ \\ H \\ O \\ H \end{array} \quad SO_2 \qquad SO_2 \Big\langle \begin{array}{l} OH \\ OH \end{array}$$

Their souls were satisfied, because the acid could be produced from sulphuryl chloride (SO_2Cl_2) and water : this proves nothing more than that it can be so made. Sulphuryl chloride often acts as a mere chlorinating agent ; years ago I argued that it was conceivable that in contact with water it gave up chlorine and that this acted as oxidising agent upon its co-partner sulphurous oxide. Sulphuric acid or rather the chlorhydrol, SO_3ClH, gives not sulphuryl chloride but pyrosulphuryl chloride, $S_2O_2Cl_5$, when subjected to the action of phosphorus pentachloride. The behaviour of the supposed second hydroxyl is peculiar : in fact, there is no proof that sulphuric acid has the symmetric structure depicted in the formula

$$HO{\cdot}SO_2{\cdot}OH$$

In its behaviour, too, the acid is not properly mindful, that this is the reputation up to which it has to live : the Batesonians would term it a facultative monogamete ; the sulphates of the magnesian series apparently are all hemi-sulphates of the type

$$HO{\cdot}X{\cdot}SO_4H$$

Only the dry elements, such as silver and the alkali

metals, insist on keeping undisturbed company with the acid radicle. Most significant of all, as Worley and I have contended and shown, the sulphonic acids generally have 90% of the hydrolytic power of sulphuric acid—and they are formed, it is supposed, by the mere displacement of one hydroxyl in sulphuric acid by a hydrocarbon radicle

$$HO{\cdot}SO_2{\cdot}OH \qquad R{\cdot}SO_2{\cdot}OH$$

In my early days, Kolbe and Würtz quarrelled over lactic acid—"The Mountain called the Squirrel little Prig." Kolbe said the acid was unibasic, though dihydric; Würtz said it was bibasic. Kolbe won the victory and it was settled for all time that the basicity of an organic acid proper was determined by the number of carboxyl groups it contains. I have thrown down my gage, in like manner, in defiance of all comers who seek to rate sulphuric acid as bibasic and I challenge a definition of basicity. Inorganic chemists to-day are but fainéant fighters: policeman Arrhenius keeps them in order still. Surely someone will adventure his skill against my light weight: if not, soon I shall claim the stakes and insist that basicity is to be defined as the number of times the characteristic acid radicle is repeated in the molecule and that sulphuric acid is but a mineralised lactic acid. The argument is equally applicable to other mineral acids (including the organic acid, carbonic acid) rated as polybasic.

It is in no wise certain even that sulphuric acid is a hydroxylic derivative: I believe it to be more probable that the original Berzelian conception, embodied in the formula

$$SO_3{\cdot}OH_2$$

may come to be regarded as the more suitable expression of its structure and behaviour. Perhaps only

carboxylic and sulphonic acids are properly represented as hydroxylic derivatives. We must always remember that our structural formulae are mainly used as shorthand expressions of actual behaviour in terms of a conventional symbolism.

Very remarkable too is the electrolytic behaviour of sulphuric solutions—in no way in accord with the tenets of the ionic school. The stable term is pyrosulphuric acid; this is almost a non-conductor. In the passage from $H_2S_2O_7$ to H_2SO_4, conductivity increases to a maximum, then falls to a minimum which is not so low as the first; it then rises to a high maximum approximately at $H_2SO_4 \cdot 4OH_2$, after which it gradually drops to zero when water is reached. No other compound is more subversive in its behaviour of the simple ionic faith but its vicious example has been quietly kept in the background. Altogether the acid is one of the most wonderful of compounds.

My theme is in no wise exhausted; I have but touched the fringes of thionism. Not a little should be said of the manufacture of sulphuric acid, of the part played by the catalyst in the anhydride process and by the determinant in the chamber process. Particularly I should like to consider, using Erasmus Darwin's melodious words—

> How nitrous gas from iron ingots driven
> Drinks with red lips the purest breath of heaven

and acts as go-between to raise sluggish sulphurous acid to corrosive rank. The neglect of nitrous chemistry by the text books is phenomenal. Something also should be said of the peculiarities of thionic activity in general and of Θειον itself but here to-day my drama must end,

although the tale of heroes to be borne by the Valkyrie across the bridge into the thionic Valhalla is incomplete. I have but given you leit-motiven, the undercurrent of melody, perhaps I should say of discord, for which the complete score has yet to be written. The support of my arguments must be given, if not in an appendix, in footnotes, a course for which I have the precedent set by the master mind of inorganic chemistry, Mendeléeff, whose fruitful service to our science we can venerate more than ever now that our countryman Moseley has placed his great imaginative work upon a solid spectral foundation and the elements are taking shape as structural units. We have reason to hold the M's in fond memory in chemistry and a special corner in Heaven or Hades might well be railed off for them—Mendeléeff, Moseley, Mond, Müller, Meldola. To-day we add Messel to their number, as the most skilful user, in our time, of an element which shares its name with the Divinity—probably the element which, as fire-stone, first attracted the real attention of man, if not the foundation stone of chemical science.

During over fifty years past, as I have watched the progress of chemistry, the advance of the organic workers has been steady and a monumental industry has grown out of their labours: the building is there upon impregnable foundations, only a few towers and turrets and features of ornament remain to be added. The foundations are of surprising simplicity—those laid by Frankland and Kekulé, not forgetting Pasteur—but they were well and truly laid and have been duly and honestly built upon.

In other branches of chemistry, however great the cackle and whatever fuss may have been made, no corresponding progress can be recorded; the progress has

been chiefly on the practical side. There has been little conscious, systematic effort to develop a theory of chemical change; the unassailable foundation laid by Faraday has in no way been properly extended. The careless methods of Society have been made the methods of a pretentious science. The growth of fact has made us mere worshippers of facts—and, as I have already said, the teacher has taken the place of the learner and the teacher can but follow fashion. Whilst claiming to be members of a scientific fraternity, we are not sufficiently developing and using scientific method.

It is only necessary to glance at books like Mellor's comprehensive Treatise or Bayliss's great work on General Physiology to realise the be-muddled condition of our subject. Fortunately there is evidence of a return to an eclectic philosophy, to what Jacques Loeb naïvely calls "the classical chemistry as contrasted with Colloid Chemistry," exemplified by Loeb's own praiseworthy efforts to raise the character of the proteins from mere indeterminate lumps of jelly to a status of definite materials behaving in a simple and definite, orderly manner, if only put under comparable conditions: then all the rodomontade of the glue-stuff school can be put aside and translated into a few common-sense, simple propositions.

Let us recognise that Chemistry is Chemistry, one and indivisible; let us put all pretence aside and abolish sects and sectarianism:

Il faut cultiver notre jardin

If I quote from *Candide*, following the example of that most delightful of Bohemians, whose name alone should recommend him to Catalysts, Berzélius Nibbidard Paragot, it is with emphasis upon our need *to cultivate*—

first the Cabbage Patch, the vegetable section, which will give us all necessary advitants. If we be good gardeners, the flowers will follow naturally and will be well placed. Let us, however, always give care to the garden as a whole, that all be well ordered in it, planted in due season; never over-fertilised and so made to yield overgrown fruit of poor flavour and substance, as is too much of our modern produce; constantly tilled and weeded most carefully, this last especially: then will it yield crops in full measure and of good quality.

"By our proficiency we know that we are in the way to heaven, as we know a tree is alive by its daily growth."

THE ORIGIN OF OSMOTIC EFFECTS

HYDRONODYNAMIC CHANGE IN AQUEOUS SOLUTIONS

From 1885 onwards, in communications to this Society and elsewhere, I have advocated an electrolytic explanation of chemical change, reciprocally a chemical explanation of electrolysis, in which no assumption is made beyond the ordinary canons of chemical belief. I have reason to think that, even now, my conception is in no way understood. I also can but recognise that I have not yet presented my full case.

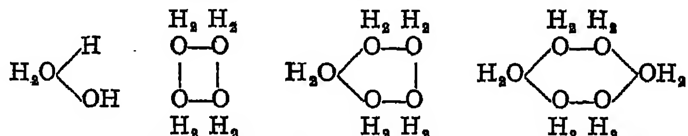
The following statement is an attempt to show that a simple explanation may be given of the operations involved in the dissolution of "salts" in water, of the same mathematical form as the ionic dissociation hypothesis, accounting equally well for electrical and osmotic peculiarities, which has the advantage that it is in harmony with general chemical experience. Although in most part but a repetition of arguments already advanced, the statement is more comprehensive and definite than any previous attempt; the consequences, particularly with respect to water, may prove to be not without application in other fields of inquiry.

Much of the difficulty, in any theoretical advance, is due to the force of prejudice and of dictated belief.

The great obstacle, apparently, in arriving at an acceptable solution of the problem of chemical change (including electrolysis) has been the constant association of the symbol OH_2 with "water" and the disregard of the determining part played by "water"; "water," moreover, has an undeserved reputation for "neutrality." Actually, the symbol is only representative of the molecule in dry steam. The term water should be confined to the liquid. To give emphasis to this contention, I have applied the name *Hydrone** to the simple unit-molecule symbolised as OH_2, choosing this ketonic term advisedly, instead of *Hydrol*, because of the special significance of *ol* in chemical nomenclature.

My one postulate is, that not only are electrolysis and chemical change inseparable reciprocal effects—the conditions which determine the one inevitably involve the other—but that change takes place and only takes place in a system of three components, such as is known to constitute a voltaic-couple.

The picture I would draw of water and of aqueous solutions is as follows. Water is a complex mixture, in proportions which vary with the temperature, of the fundamental molecule, *hydrone* (OH_2), with molecules of various polymorphs, perhaps.

1. 

Hydronol Tetrhydrone Penthydrone Hexhydrone

Hydrone is the volatile component of water and the vapour-pressure may be regarded as the relative measure of the proportion in which it is present. Whether the liquid contain any other directly volatile constituent is an

* "Hydrolysis, Hydrolation and Hydronation as Determinants of the Properties of Aqueous Solutions," *Roy. Soc. Proc.*, A, vol. 81, p. 80 (1908).

open question: as the relative density of the vapour from (not of) water is greater than 9 near to the boiling point, some molecules of greater mass than that of hydrone are contained in the gas (*cf.* Menzies, *J. Am. Chem. Soc.*, 1921, 43, 851).

The proportion of hydrone molecules in ordinary water must be small. If water were but a collocation of molecules of hydrone, the boiling-point of the liquid would be far lower—its freezing point would also be much lower. Even if it contained any considerable proportion of hydrone molecules, its boiling point would be lower.

If any substance be dissolved in water, the physical properties of the liquid are proportionately altered, not always in the same molecular ratio but to an extent which depends upon the nature of the compound dissolved; potential electrolytes produce the greater effect per molecule. Apparently, the effect is in no way mechanical, *i.e.*, solvent and solute do not merely become mixed together and the molecules separated by mutual (mechanical) interference; the process is inductive and chemical throughout.

Non-electrolytes all produce the same effect per molecule, whatever their molecular magnitude, in raising the osmotic attractive power of water and, at the same time, of lowering its vapour pressure. The negative pressure developed within the liquid is such that apparently a gramme-molecular-proportion of hydrone is *taken out of action as volatile constituent* per gramme-molecular-proportion of the *non-electrolyte* dissolved; each molecule of the solute appears to "anchor" a molecule of hydrone,*

* This is the conclusion Poynting came to in 1896 (*Phil. Mag.*, vol. 42, p. 298). Poynting was a convinced advocate of the view that association, not dissociation, is at the root of osmotic phenomena. The fact that complex hydrates are often formed seems to have been the chief reason why his view did not find greater favour (compare Callendar, *Roy. Soc. Proc.*, A, vol. 80, p. 481 (1908).

yet in some special way which enables this still to preserve its attractive power for molecules of its own kind. The effect of potential electrolytes is greater, to an extent depending upon the valency and character of the constituent radicles; "salts" of the type X′R′, in very dilute solution, may produce an effect double that proper to a single molecule and the effect of salts containing radicles of higher valency than unity may be still greater.

Solutions of such "salts" are electrolytic conductors and chemically are not only active but, when two salts in a solution (a reciprocal salt pair) interact (the Williamson change), the change is practically immediate in its occurrence.

No binary hydrogen compound in the liquid state is an electrolyte *per se*. The facts are such that we are justified in assuming that compounds such as hydrogen chloride and hydrone, in the liquid state, would be without trace of conductivity and inactive chemically, *if pure*—although, probably, water, as we know it, would then have no existence. I use the word pure in the ideal sense of free from impurity, recognising no degrees of purity but only of impurity.

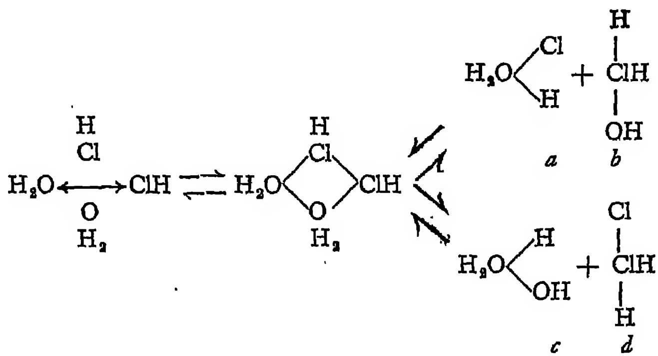
How, then, does conductivity arise when hydrogen chloride is dissolved in water? Even the two simple molecules (both potential electrolytes) would not *interact* when in contact; at most, it may be supposed, they would merely

2. $$HCl \longleftrightarrow OH_2$$

form a couple in which they exercised an inductive attractive effect (contact difference of potential) upon one another but nothing more. Such an effect might cause the withdrawal (neutralisation) of hydrone (the fall of vapour pressure is evidence of such fixation) but the

osmotic activity acquired by the solution cannot well be accounted for by the occurrence.

Suppose, however, that a conducting circuit could be and were formed by the conjunction of such a couple with the two independent molecules and that electrolytic change took place; this might be of the following order:

3. 

If it cannot be admitted that a voltaic couple could be thus constituted, the intervention of some third component must be postulated: if not an "impurity," the walls of the containing vessel, alternatively, *dissolved gas*, may be called into service and should suffice.

The extent to which change takes place reversibly, in the two directions indicated, must be left open to decision. The production in electrolysis of chlorine alone from strong solutions but together with oxygen from weak solutions may conceivably be due to the preponderance of system *d* in the former. The rapid increase of the assumed "molecular" conductivity of the hydrogen chloride, as the concentration is diminished, however, is an indication that the more steady state *a b*, eventually *a c*, is rapidly reached.

In these electrolytic changes the primary molecules

engaged would be *distributed* upon one another. In the reciprocal complexes thus formed, the affinity of the constituent radicles, *inter se*, would be less strong than in the original simple molecules: thus the chlorine would be but weakly held by the oxygen in the muriated complex *a*, the hydroxyl but weakly by the chlorine in the hydrol *b*. On the other hand, the residual affinity of the chlorine atom would be greater than that of chlorine in hydrogen chloride and that of the oxygen in the hydrols greater than that of oxygen in hydrone. Each such distributed system would be eminently attractive to hydrone.

If change take place in the manner suggested, the number of " distributed " active systems produced can only be equal to the number of molecules of the solute: some further change must therefore be postulated to account for the ultimate apparent " doubling " of the molecular influence of the solute—for the enhanced effect produced by the potential electrolyte.

Assuming that change took place to an ever-increasing extent, as the solution became more and more dilute, in a direction involving the rupture of the " couple " shown along the dotted lines in the following equation,

$$4.\quad \begin{array}{ccc} \mathrm{ClH} & \vdots\ \mathrm{OH} & \mathrm{H} \\ \cdots | & \cdots\cdots\cdots\cdots & | \cdots \\ \mathrm{H_2O} & \mathrm{HO}- & \mathrm{ClH} \\ | & & \vdots \\ \mathrm{H} & & \vdots \end{array} = \mathrm{H_2O}\left\langle\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\end{array}\right. + 2\mathrm{ClH} + \mathrm{OH_2},$$

hydronol would be formed in an increasing proportion relatively to the hydrone chloride *a*.

In a sufficiently dilute solution, ultimately, two osmotically active, reciprocal molecules would be produced, at the expense of each single molecule of the chloride: in other words, the single molecule of the potential electrolyte, hydrogen chloride, would apparently

have double the effect of a single molecule of a non-electrolyte.

Assuming that electrolysis involve the interaction of two diverse "distributed" systems, under the influence of an electromotive force, the (molecular) conductivity of the dissolved chloride would also be at its maximum in the fully diluted liquid.

The formation of the all but neutral polyhydrones present in water together with the highly active molecules of hydrone and hydronol is to be pictured as taking place in a similar manner, by condensation from several molecules of hydrone, under the influence of the primary distributed systems discussed above. Apparently, molecules of hydrone, like atoms of carbon, have a natural tendency to "fall or fit together" in certain ways, which may well be similar. In fact, if the carbon atom be represented by a pyramid of four equal spheres—corresponding with its quadrivalency—the molecule of hydrone may be represented by a like model in which two of the spheres are taken to represent the oxygen atom and the other two the two hydrogen atoms.

A similar structure may be assigned to the metallic ammonias without assuming that the metal in these compounds has a specially high valency. The partial or complete inertness of the negative radicle in many of these is better explained in this way than by current assumptions.

The distribution of a substance in water, in the manner set forth, must involve a reduction in the proportion of hydrone molecules. That fresh molecules are supplied to take their place by dissociation of the polyhydrones is not to be supposed, as vapour pressure falls as the solution becomes more concentrated ; apparently, the polyhydrones are hydrolysed and reduced to hydrone

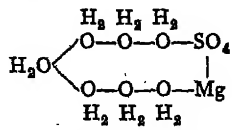
only in response to the demand made when the proportion of salt is increased.* It follows that the composition of the "water" in a solution must vary not only as the temperature changes but also with the concentration—the relative proportions in which the several constituents are present must be changed.

That the affinity of the solution for hydrone increases with the concentration is clear, however, from the increase in osmotic activity. This osmotic activity is to be attributed, as indicated above, to the reciprocal distributed systems: in a dilute solution of hydrogen chloride, for example, to the molecules of muriated hydrol and of hydronol, $\mathrm{HCl}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OH}\end{smallmatrix}$ and $\mathrm{H_2O}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OH}\end{smallmatrix}$

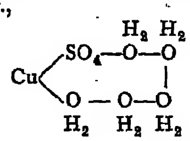
Each such system has unit effect: if the solution be placed in contact with water, molecules of hydrone are attracted from the water, one molecule by each unit system, the result being that the complex is held in check and neutralised.

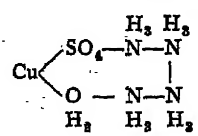
The pressure is exercised by the hydrone molecules thus controlled. In other words, the osmotic pressure is due to the directed oscillatory impacts of molecules of hydrone, not of molecules of the dissolved substance: it

* Opportunity may be taken to point out that the water of crystallisation in salts may well be of the polyhydrone form—in the sulphates of the magnesium group, for example:



Ammonia would seem to take the place of hydrone in the complex ammonia salts, *e.g.*,





is rather to be regarded as of the order of hydraulic than of gaseous pressure.

The most striking fact in connection with the behaviour of non-electrolytes is their unit-effect per molecule. Thus the osmotic effect of a molecule of alcohol, $C_2H_5 \cdot OH$ is the same as that of the complex molecule of cane-sugar, $C_{12}H_{14}O_3(OH)_8$. The influence of the molecule is, in a sense, polar: apparently it is exercised from a single centre. Some inductive influence is at work, in the complex hydroxy-compound, preventing effective hydrolation at contiguous hydroxy-groups and favouring it at some one dominant centre—perhaps at the etheric linkage between the two C_6 complexes.

This conception must be extended to other solvents in which no "distributive" action is possible, which develop no special activity in the dissolved substance such as is produced on dissolving electrolytes in water. All solvents probably are to be regarded as mixtures of simple molecules with complexes formed by the association of several of these units. The proportion of simple molecules present must be a fixed one in every liquid and if equilibrium be disturbed by the fixation of the unit molecule by that of the solute the solution will be attractive of such molecules to the extent required to meet the deficiency.

As the interacting molecules in an aqueous solution are the complexes formed primarily from molecules of hydrone, the variations in the rate of change, not only as the composition of the solution is varied but also as the temperature is varied, will be proportional to the number of molecules of hydrone available. The conclusion arrived at by Adrian Brown and Worley* that the variation in the entry of "water" into the barley grain

* "The Influence of Temperature on the Absorption of Water by Seeds of *Hordeum vulgare* in relation to the Temperature Coefficient of Chemical Change," *Roy. Soc. Proc.*, B, vol. 85, p. 546 (1912).

is coincident with the variation in the vapour-pressure of water—*i.e.*, the proportion of escaping molecules of hydrone—is in harmony with this assumption. It also provides an explanation of the uniform variation of the rate of chemical change in solution enunciated by Harcourt and Esson,* expressed by the relation

$$K/K' = (TT')^m,$$

KK′ being the rates of change at absolute temperatures TT′ respectively, m being a number peculiar to each condition of change which expresses the ratio of dK/K to dT/T. This was originally stated by them in 1895 in the form

$$\frac{K_t}{K_0} = \left(\frac{273 + t}{273}\right)^m$$

and is obviously but the gas law in disguise.

We are in no way at the end of the study of liquids. H. B. Baker's recent observations on the effect of drying benzene very thoroughly in raising its boiling point are an indication that the properties we are in the habit of assigning to liquids may be, in a considerable degree, influenced even by a minute impurity. In all liquids change of state involves chemical change.

Water in particular has still to be appreciated. If the influence of a "salt" in determining change be as suggested, the production of water from hydrone—being a chemical process—is dependent upon the presence of a potential electrolyte: there would be no condensation of the gas in the absence of such a conditioning agent. It has long been held, on the basis of Aitkin's observations, that the formation of raindrops in the upper atmosphere is due to the presence of nuclei. The sup-

* *Phil. Trans.*, ser. A, vol. 212, p. 187 (1913).

position was at first made that these might be mere dust particles; of late meteorologists have contended that only "hygroscopic" materials are effective as nuclei. It is safe to assert that the nucleus must be a potential electrolyte.

The electrical discharge developed in the division of large drops—apparently the origin of thunderstorms—may be regarded as the consequence of a change in the composition of the water as the drop divides. The evaporation from a drop is said to be in excess of that from the same plane surface, the more the smaller the drop.* If this be so, it may be supposed that the proportion of hydrone is greater in drops than in a mass of water and that the proportion is the greater the smaller the drop. Attention has been drawn by G. C. Simpson † also to the presence of water drops in the upper atmosphere at temperatures far below the freezing-point of ordinary water; maybe this is possible, because the "water" in such drops, being different in composition from ordinary water, richer in its volatile constituent hydrone, is less easily frozen. This same argument is probably of consequence—at least to be kept in mind—in any discussion of the influence of moisture in chemical change at catalytic surfaces, particularly in cases in which a certain critical minimum proportion has maximum effect.

I have spoken of *pure water* as an ideal which cannot be realized, because of the impossibility of excluding impurity and of condensing pure hydrone. If pure water were obtained, it would be different from the water we know in not a few particulars.

The conclusions arrived at in this communication are summarised in the following propositions:

* Sir Wm. Thomson, *Phil. Mag.* [iv], vol. 42, p. 448 (1871).

† *Nature*, April 14, 1923.

1. "Water" is a complex saturated with the "gas", *hydrone*, OH_2. Primarily, hydrone is the sole potentially "active" constituent but it becomes actually active only under conditions which suffice to determine electrolytic change. Pure water would be inert—but this is and must ever be an ideal.

2. The vapour pressure either of water or of a solution is the measure of the proportion of *free* hydrone molecules present in the liquid. The diminution of the pressure when a substance is dissolved in water, therefore, is a proof that the molecules of hydrone are concerned in the change and are thereby diminished in proportion.

3. Although the vapour pressure is lowered in presence of any solute, the solution acquires attractive properties. The internal activity is increased whilst external activity is diminished. Non-electrolytes all have unit effect per molecular proportion; potential electrolytes have at least twice this effect, in sufficiently dilute solutions.

4. The effect produced may be ascribed to an interaction of molecules of the solute and those of hydrone. From non-electrolytes (under the influence of conducting impurity) a simple hydrol is formed, $M<^{H}_{OH}$, only a single molecule of hydrone being "distributed" upon the molecule of the solute, whatever its magnitude.

5. In the case of potential electrolytes, a reciprocal interchange of the radicles of the salt and of hydrone is to be postulated. Not only is the solute hydrolated but it is itself distributed upon hydrone, the salt $\overset{+}{R}'\overset{-}{X}'$ giving rise initially to the reciprocal systems

$$RX<^{H}_{OH} \quad \text{and} \quad H_2O<^{R}_{X}$$

6. As the concentration is lowered, under the influence

of hydrone, the complex $RX{<}^{H}_{OH}$ is more and more converted into hydronol, $H_2O{<}^{H}_{OH}$. Ultimately the solution contains the solute only in the form $H_2O{<}^{R}_{X}$, together with an equal number of molecules of hydronol. The solute then has maximum (bimolecular) effect.

7. The "distributed" reciprocal complexes, including hydronol, are the electro-chemical agents in a solution. The negative radicle in such complexes has greater residual affinity than it has in the original simple molecules; it is specially attractive of hydrone and, therefore, hydrone is attracted into the solution when it is in contact with water.

Each complex attracts a single hydrone molecule, the molecules thus brought into the solution serving to restore the hydrone equilibrium.

8. The osmotic pressure manifest in an aqueous solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the distributed complexes, one by each complex, acting as though they were present in the gaseous state. In short, the osmotic pressure developed within an aqueous solution, whatever the solute, has its origin in one and the same cause and is properly spoken of as *Hydronodynamic*—if the word be permissible; indeed, this term may be used as expressive of the general activity of water, *electro-chemical and osmotic.*

ELECTROLYTIC CONDUCTION

SEQUEL TO AN ATTEMPT (1886) TO APPLY A THEORY OF RESIDUAL AFFINITY

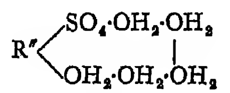
In discussing the phenomena of electrolytic conduction, in March, 1886,* I drew a distinction between simple and composite electrolytes, the former being salts such as the silver haloids, the latter, mixtures of compounds which are themselves dielectrics. Only metallic salts of certain types are simple electrolytes: thus no *per*-salt is a conductor. At the time we had little knowledge of the exact behaviour of simple electrolytes, so that my treatment of the subject could only be tentative and provisional. Even now the conducting salts are insufficiently studied but from what has been learnt in the interval it is becoming clear that their structure is the determining factor.

Mercuric chloride seems not to be an electrolyte, even in conjunction with water. Some salts, those of cadmium, for example, are very weak electrolytes and exert but a slight "excess" influence; these probably are but slightly "hydrolysed" in solution and for the most part simple "hydrolated," like non-electrolytes.

The sulphates of the magnesian group are also relatively

* "Electrolytic Conduction in Relation to Molecular Composition, Valency and the Nature of Chemical Change: being an Attempt to Apply a Theory of Residual Affinity, *Roy. Soc. Proc.*, vol. 40, p. 268 (1886).

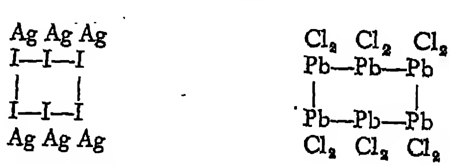
insensitive, the effect they produce being only about the same as that of a simple salt of the X′R′ type. The nitrates and chlorides of the same metals are more active. The unsymmetrical character of sulphuric acid is not yet sufficiently recognised, nor is it realised that it behaves essentially as a monobasic acid. If the magnesian sulphates be closed systems of the type



they may not be even potential electrolytes and only act as such when dissociated by hydrolysis.

Of special interest, from this point of view, are the silver and lead haloids; we are indebted to Tubandt * for an exact study of the behaviour of several of these in the heated solid state. Silver iodide, bromide, chloride and fluoride and lead chloride and fluoride are good conductors and strictly obey Faraday's law; but whereas the silver compounds are so affected that silver is deposited at the one electrode and withdrawn from the other in equal amount, the lead haloids abandon halogen to the one electrode and take it from the other.

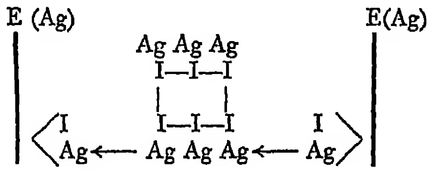
In popular parlance, the current is carried by the metallic ion in the electrolysis of the one and by the non-metallic in that of the other. The difference cannot well be interpreted except by the assumption that the two classes of salt differ in structure, perhaps in some such manner as shown in the formulae—



* *Zeits. anorg. Ch.*, vol. 115, p. 105 (1921).

Assuming that the explanation of electro-chemical change and of osmotic effects stated in the previous communication ("Origin of Osmotic Effects,") be applicable to such compounds, the primarily active unit is the fundamental molecule AgI in silver iodide and $PbCl_2$ in lead chloride. The haloids will contain these units in proportions which vary with the temperature.

Let it be assumed that one or more of these primary units be *distributed* at each electrode and that a circuit be formed by these molecules becoming coupled with the complex molecules, as shown in the following scheme :



It is easy to see that, if the metallic atoms move with the current and the silver atoms distributed at the two electrodes be forced into circuit at the one and laid down upon the other, the two iodine atoms originally associated with them will be in a position, the one to take an atom of silver from the silver electrode face, the other to combine with the silver atom carried by the current to the opposed electrode. In this way, the supply of the distributed unit molecules would be constantly maintained at the electrode surfaces. The molecular conductivity would depend upon the number of such active units in circuit at the electrodes.

A precisely similar explanation may be given of the behaviour of lead chloride, the difference being that in this compound the chlorine atoms, not the metallic, are at the "surface" of the molecule.

This interpretation of the process may be equally applied

to the electrolysis of aqueous solutions. In these, the reciprocal complexes I have postulated may be thought of as distributed upon the electrode surfaces and electrolysis as taking place owing to interactions, at the electrode face, affecting these and the other similar molecules in the solution with which they became linked. In aqueous solutions, however, both ions circulate and often, if not always, at least the negative ion carries a burden either of hydrone or of a polyhydrone. Again molecular conductivity would be determined by the number of units effectively distributed upon the electrode surface.

In all solvents other than water, probably complexes are formed and conductivity is due to the interaction of these and the distributed primary molecules of the solute. On such a view, it is conceivable that, in aqueous solutions, the complex polyhydrone molecules enter into the circuit but act metallically, only yielding up hydrogen atoms: hence, perhaps, the superior velocity of the hydrogen ion.

The influence of salts and non-electrolytes upon conductivity and other properties of aqueous solutions—a subject of great complexity—has yet to be discussed. It is already clear that "corrections" must be introduced corresponding with those made by Van der Waals in dealing with pressure and temperature effects in gases.*

* "Studies of the Processes Operative in Solutions.—XXIX. The Disturbance of the Equilibriums in Solution by 'Strong' and 'Weak' Interfering Agents." By H. E. Armstrong and E. E. Walker, *Roy. Soc. Proc.*, A, vol. 90, p. 375 (1914).

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